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Vladimir N. Kholodov

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**A Journal on Problems of the Theory of
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Lithology and Mineral Resources

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Lithology and Mineral Resources (Litologiya i Poleznye Iskopaemye) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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Hypotheses of Phosphogenesis and Oceanic Environment

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Received December 7, 1998

Abstract—Both former and contemporaneous ideas concerning mechanisms of phosphogenesis, including the biogenic, chemogenic, and volcanogenic mechanisms, are reviewed. Major specific features of Recent and Late Quaternary phosphogenesis on Namibian and Peru–Chilean shelves, which are the locations of the most active coastal upwelling in the ocean, are described. Phosphogenic hypotheses are compared with the Recent phosphate accumulation process, helping to reveal their resemblances and differences. It is concluded that Recent phosphate accumulation inherited some of its characteristic peculiarities from previous phosphogenic episodes in ancient oceans.

INTRODUCTION

The origin of phosphorites, which are characterized by a strong variability of lithological types and deposition environment, has been disputable since their first finding in Cretaceous sedimentary sequences of England in the beginning of the 19th century. During the elapsed time period (over 150 years), a series of various phosphogenic hypotheses have been suggested, most of which accept that large phosphorite deposits had been initially related to the marine environment.

Because of this, it seems reasonable to discuss whether these ideas, schemes, and models, which we shall call hypotheses for convenience, are compatible with recent knowledge in the realm of oceanology, marine geology, and geochemistry.

Traditionally, phosphogenic hypotheses are divided into three groups—biogenic, chemogenic, and volcanogenic—depending on the factor considered as predominant. However, a number of new hypotheses have appeared of late, which include some original ideas, whereas others still comprise certain basic elements of preceding hypotheses. Let us consider their essential features.

PHOSPHOGENIC HYPOTHESES

Biogenic Hypotheses

Biogenic hypotheses are based upon assumption that the accumulation of phosphate is directly related to biogenic materials or products of organic metabolism.

According to the first biogenic hypothesis suggested by Buckland (1829), phosphatic nodules in Cretaceous deposits were in fact phosphatized coprolites of reptiles and other animals which at the time provoked many humorous comments (Notholt, 1981).

Sometime later, in 1845, Russian geologist A.A. Kaiserling passed along idea that phosphorites in the Kursk region were formed by the redeposition of

calcium phosphate, provided by bones of dead organisms. Following the discovery and investigation of Albian and Upper Cretaceous phosphorites in France and Belgium, a number of investigators came to the same conclusion in regard to the biogenic phosphorus source (C. Lyell in 1855, A. Daubré in 1868, F. Cornet in 1886).

However, the most detailed biogenic hypothesis was offered by J. Murray and A. Renard (1891) after the first combined oceanographic expedition on the HMS *Challenger* (1872–1876), which found phosphorites on the sea floor near the South African coast. According to their hypothesis, phosphogenesis is related to the mass mortality of marine fauna, mainly fishes, in areas where cold oceanic currents meet warmer ones; subsequently, the formation of phosphatic nodules proceeds, owing to liberation of phosphorus from biogenic matter, and its deposition in sediments below the water–bottom interface. This hypothesis, later called “biolithic,” remained dominant during a long period of time and was accepted by Russian geologists such as A.D. Arkhangelskii and Ya.V. Samoilov, who discussed this problem in several papers published in 1909–1923 years.

Some adherents of this hypothesis, including Arkhangelskii, stressed that the accumulation of phosphate is related to transgression–regression cycles and redeposition of sedimentary material (Strakhov, 1971). Based on investigation of North African phosphorites, they suggested the concept of biolithic diagenesis or metasomatic phosphatization of calcareous materials in bottom sediments as described by A. Carnot, F. Cornet, G. Kredner, L. Chateau, L. Pervinquer, L. Kraft, and L. deLonnet in their papers published during the late 19th–early 20th centuries.

Later, G.I. Bushinskii (1963, 1966, 1967) suggested his original biochemical variety of biogenic hypothesis. Stressing the dominant influence of river runoff, he opposed the idea of mass mortality-dependant phosphogenesis and assumed that phosphorus accumulation

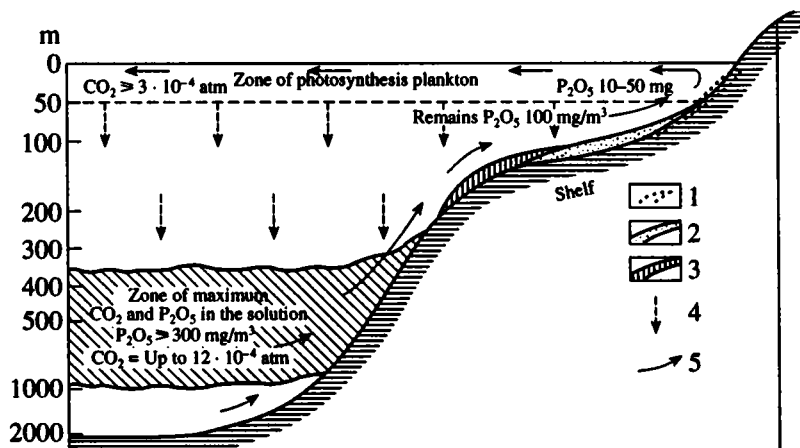


Fig. 1. Phosphogenic model after Kazakov (1939). (1) Facies of near-shore gravels and sands; (2) phosphorite facies; (3) facies of calcareous sediments; (4) sedimentation of planktonic remains; (5) current direction.

in sediments is not rare but rather a routine process driven by the permanent deposition of planktonic detritus upon the sea bottom. According to his opinion, most phosphatic grains in phosphorite deposits were originally coprogenic. Moreover, he considered enzymatic processes to be major stimulators of phosphorus concentration in various environments, even where physicochemical conditions are unfavorable for such a process.

The major branch of biogenic hypotheses was supplemented with the microbiological variety developed in the beginning of the 20th century, first formulated by E. Blackwelder (1916), who assumed that biolithic diagenesis is related to the anaerobic bacterial degradation of phosphorus-bearing organic remains. In the course of time, this notion was transformed into the idea that bacteria concentrate phosphorus directly from marine environment and their vital activity itself might induce phosphorite formation as evidenced by numerous bacterial or rather bacteria-like particles (Kassin, 1925; Cayeux, 1936). This hypothesis is supported by a number of recent researchers demonstrating microphotographs of such particles (O'Brian *et al.*, 1981; Lucas, Prévôt, 1984, 1985; Mirtov *et al.*, 1987; Zanin *et al.*, 1987; Rao, Nair, 1988; Lamboy, 1990; Rao *et al.*, 1992; Soudry, 1992, 1993).

Chemogenic Hypothesis

The chemogenic hypothesis, postulating the chemical deposition of calcium phosphate from sea water, is associated primarily with A. V. Kazakov's name, but his predecessors were American geologists D. Condit, E. Finch, and A. Pardee (1928), who suggested that the chemical origin of Phosphoria Formation phosphorites is due to calcium phosphate fallout in the course of evaporation of regressive basin.

According to Kazakov (1939), calcium phosphate is deposited not in evaporating but in normal marine

basins. His major idea consists of an upwelling of phosphorus- and carbonic acid-enriched water (about 1000 m deep) reaching the shelf area where CO_2 diffuses into the air, whereas calcium phosphate falls out owing to an increase in alkalinity and a warmer temperature (Fig. 1).

After Kazakov's hypothesis, others appeared relating phosphate accumulation to the chemical processes in a water body or near the water-bottom boundary.

To explain the known phenomenon of limestone phosphatization, a metasomatic hypothesis was suggested based on laboratory experiments imitating carbonate to a phosphate replacement in the course of limestone and sea water contact (Ames, 1959). This hypothesis was specifically implied for the interpretation of phosphorite genesis on the Pacific submerged mountains whose slopes have been washed by waters depleted in oxygen and enriched in phosphorus (Hein *et al.*, 1993).

The hydrogen sulfide-biogenic hypothesis relates phosphogenesis to the accumulation of phosphorus in waters of hydrogen sulfide basins; in the case of aeration, these waters eliminate excess phosphorus, which is metasomatically replacing organic matter or falling out onto sea bottom (Kholodov and Paul, 1995a, 1995b; Kholodov, 1997).

The phosphatic pump trap hypothesis was suggested by a group of investigators relative to phosphogenesis on the Peruvian shelf (Froelich *et al.*, 1988). According to this hypothesis, iron hydroxides adsorb dissolved phosphorus from bottom waters and carry to the sea floor. After the burial in sediments, they are reduced and then release phosphorus, which precipitates, in the form of calcium phosphate. Meanwhile, reduced iron diffuses into near-bottom water, and after being oxidized it adsorbs a new portion of phosphorus subject to subsequent precipitation (Fig. 2).

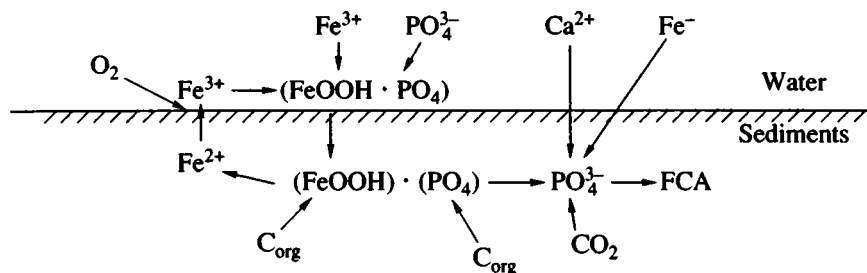


Fig. 2. Model of the phosphatic pump trap, after Froelich *et al.* (1988). (FCA) fluorcarbonateapatite, which is formed owing to the separation of PO_4^{3-} from iron hydroxides.

The original convection-diffusion hypothesis, of the phosphorus supply from bottom waters to sediment, was suggested by K. Föllmi and R. Garrison (1991). Using the theoretical models of other authors (Morse, 1974; Boudreau, Guinasso, 1982) they came to the conclusion that dissolved phosphate may migrate from bottom waters to sediment, owing to the diffusion process helped by the near-bottom current. According to Föllmi and Garrison, such a mechanism may provide a rate of phosphate layer accumulation on the order of 0.01 mm/ka. This is suggested as the interpretation of the origin of phosphatic crusts and phosphatized hardgrounds.

Volcanogenic-Hydrothermal Hypotheses

Several versions of volcanogenic-hydrothermal hypotheses have been suggested since the 1880s.

In 1887, the idea that phosphorites from the Somme region are of hydrothermal origin was first suggested by the French geologists M. Levy and M. Mercé. Later, in 1921, the German geologist I. Weigelt related this hypothesis to phosphorites of Estramadura in Spain, Lanse phosphorites in Germany, and aluminophosphates of the Antilles Islands. In Russia, the idea of the hydrothermal origin of Antonovo-Lipovsk phosphorites in the Urals was supported by M.I. Kantor in his work published in 1929. However, the most popular was the hypothesis of "distant volcanogenic ore formations" suggested by N.S. Shatskii (1955), who assumed that the volcanogenic phosphorus was transported by currents to distant areas where favorable conditions for its deposition exist.

During recent years, volcanogenic-hydrothermal hypotheses were proposed speculating the phosphorite origin of submerged mountains in the Pacific Ocean. This topic was motivated specifically by information about the light isotopic composition of oxygen in these phosphorites as an indication of a high environmental temperature (Safonov, 1982; Strizhov *et al.*, 1985).

At the same time, the suggestion of the phosphorite origin for the Pacific Ocean atolls is based on the Endo-upwelling Hypothesis (Rougerie, Wauthy, 1986, 1993). According to this hypothesis, relatively deep sea water

(800 m) percolates into rocks of the atoll basement, and after being heated begins to move upward thus, leaching phosphorus from drained hard rocks. Upon reaching the surface, the temperature and pressure of the solution decreases and phosphorus falls out or is extracted by bacterial mats (Fig. 3).

These major phosphogenic hypotheses related to marine environment are the basis of all our existing information. Now let us consider how phosphorites are being formed in the Recent Ocean.

RECENT PHOSPHORITE FORMATION IN THE OCEAN

Phosphorites found by the *Challenger* expedition near the South African coast and later on the Blake Plateau and in other places, appeared to be of pre-Recent age, contrary to the opinion of their discoverers. The age of these phosphorites, as revealed by radiometric dating, exceeds one million years as shown by Kolodny (1969). However, it is coincidental that the first finding of truly Recent phosphorites was reported during the same year (Baturin, 1969).

Presently, several zones of Recent and Late Quaternary phosphorite accumulations are known, including the continental margins of South and South-West Africa, Peru, Chile, Mexico, and Eastern Australia (Baturin, 1969, 1978; Baturin *et al.*, 1970, 1974; Veeh *et al.*, 1973, 1974; Burnett, 1977; Bremner, 1978; O'Brian, Veeh, 1980; Birch *et al.*, 1983; Jahnke *et al.*, 1983; Burnett *et al.*, 1988; Glenn, Arthur, 1988; McArthur *et al.*, 1988; Bremner, Rogers, 1990; Garrison, Kastner, 1990; Baturin *et al.*, 1998a, 1998b).

This process develops most actively near the Namibian coast and in the Peru-Chilean region, allowing near-continental areas of the South Eastern Atlantic and Pacific Oceans to consider as model areas for the study of oceanic phosphate accumulation.

Below is a brief review of characteristic features of the facial environment in these areas.

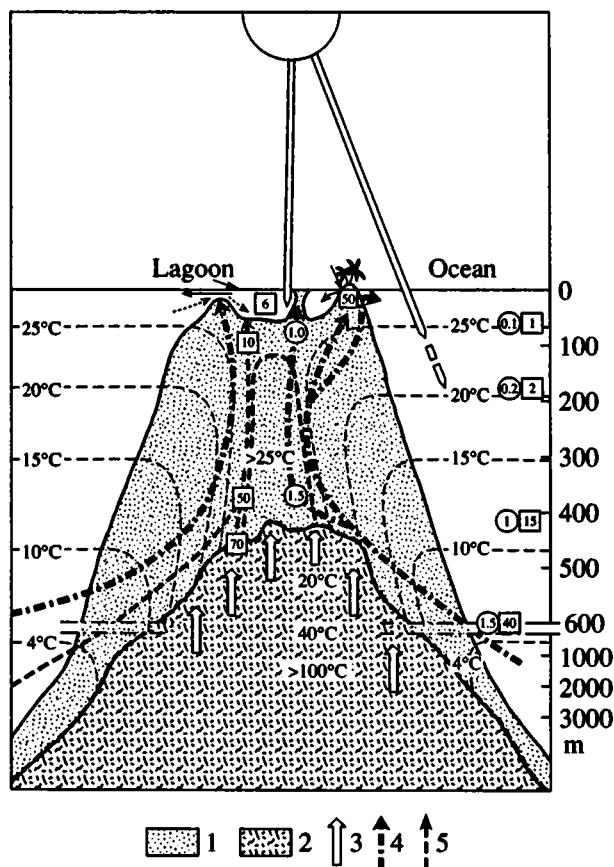


Fig. 3. Endo-upwelling model, after Rougerie and Wauthy (1986). (1) Porous coralline limestone; (2) basalt; (3) heat flow; (4) movement of dissolved silica (figures in squares depict concentration, mol/l); (5) movement of dissolved phosphate (figures in circles—concentration, mol/l).

Oceanological Setting

Shelves and upper parts of the continental slopes in both areas are washed by eastern boundary currents, which are branches of a global anticyclonic circulation system in the Southern Hemisphere (Wooster, Reid, 1963; Stepanov, 1983).

The combined action of wind and hydrophysical fields in peripheral near-shore parts of these currents produces a vertical flow component driving the upwelling of subsurface water to the shore (Fig. 4). As the permanent source of limiting biogenic elements (especially phosphorus), these waters exceedingly stimulate the biological productivity in the area, including all components of the food chain, namely, phyto- and zooplankton, fishes, marine mammalia, and sea birds (Hart, Currie, 1960). Along with maximal biological productivity, these areas are characterized by periods of episodic mass mortality of marine fauna, induced by a series of interrelated phenomena such as the disturbance of the water circulation regime, including upwelling, infection of the water body by hydrogen sulfide diffusing from bottom sediments, and the devel-

opment of some poisonous planktonic species (Copenhagen, 1953; Brongersma-Sanders, 1957).

Bottom Sediments

Owing to absence of large rivers on the nearby continent, the sediment composition in these areas is essentially controlled by the high biological productivity of surface waters. Recent sediments are represented by diatomaceous oozes and calcareous sands and silts that are mainly foraminiferal; however, in the Peru–Chilean area, the admixture of terrestrial material supplied from steep Andean slopes to the equally steep shelf and continental slope is rather essential (Saidova, 1971).

Recent biogenic sediments are, as a rule, enriched in organic matter and phosphorus. The latter can be present in various forms: as a component of organic materials or as phosphatic components proper (bone detritus, phosphatized coprolites, and diagenetic phosphatic accretions).

Terrigenous sediments in both areas are located in the near-shore zone. Phosphatic sediments on the shelf and upper part of Peruvian continental slope occur as sandy layers amidst clayey–silty muds and contain up to 40–50% of phosphatic grains predominantly 0.125–0.500 mm in size. According to radiometric dating, a portion of the grains was formed during the Holocene, whereas another portion was formed in Late Quaternary time (Burnett *et al.*, 1988).

On the Namibian shelf, phosphatic deposits are represented by a layer of phosphatic shelly sands of Pleistocene to Pliocene age whose tentative resources may reach 4 Gt of P_2O_5 (McArthur *et al.*, 1990; Bremner, 1992). The average chemical composition of Namibian shelf sediments is shown in Table 1.

Formation of Diagenetic Phosphate

The formation of diagenetic phosphate proceeds in the upper layer of sediment near the water–bottom interface, owing to supersaturation of pore water in calcium phosphate, as evidenced from combined lithological and geochemical investigations (Baturin, 1978; Froelich *et al.*, 1988; Glenn, 1990). Initially, phosphate fell out as a semiliquid gel. In diatomaceous oozes of Namibian shelf, it is represented by small particles (up to 1–2 mm), as well as by relatively large (up to several centimeters) formless or lenticular inclusions differing from the enclosing greenish gray sediment by a yellowish tint and a somewhat denser consistency. Subsequently, these accretions are subject to lithification and further phosphatization accompanied by self-purification of phosphate from nonphosphatic components, especially biogenic opaline silica. Finally, dense phosphatic grains and nodules are formed, which are comparable by their surface appearance to ancient phosphorites (Baturin, 1969, 1978; Mikhailov *et al.*, 1972). The evolution of chemical composition of these accretions is shown in Table 2.

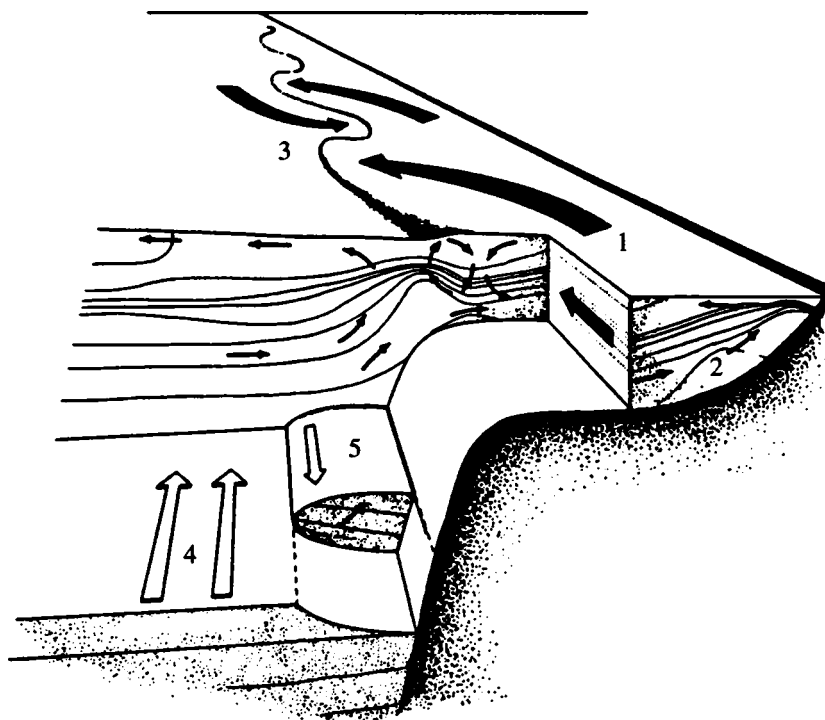


Fig. 4. Scheme of coastal upwelling, after Hart and Currie (1960). (1) Surface coastal current; (2) coastal upwelling; (3) open ocean water; (4) deep water; (5) deep compensation current.

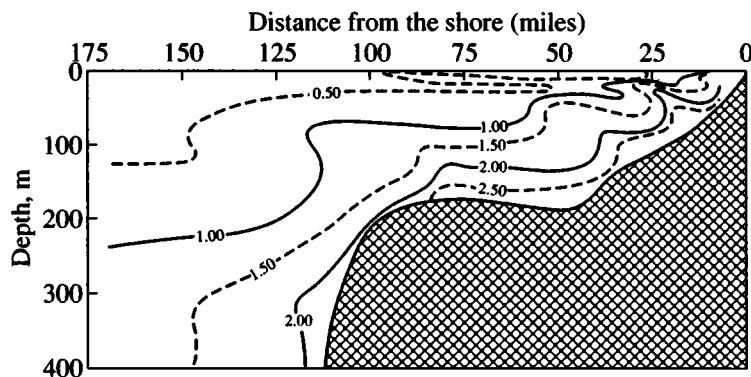


Fig. 5. Supply of phosphorus into the photic zone by upwelled water, after Hart and Currie (1960). Distribution of dissolved phosphates ($\mu\text{g atoms/l}$) across vertical section near Walvis Bay at $22^{\circ}40' \text{ S}$;

The formation and lithification of such accretions may proceed relatively fast, during several years, as evidenced by the coexistence of lithified and unlithified species from the same grab sample of upper sediment layer, whose age does not exceed several years (Baturin, 1969, 1978; Veeh *et al.*, 1974). This phenomenon is also demonstrated by the Recent age of diatoms found inside these accretions (Baturin, 1978). Formation rates of phosphatic pellets from the Peruvian shelf, separately determined by uranium series isotopes and AMS ^{14}C method in phosphatic, organic, and carbonate fractions, were also found to be similar, i.e., on the order of several years (Burnett *et al.*, 1988).

The mechanism of calcium phosphate deposition from interstitial solutions is governed evidently by the vertical alkalinity gradient. Owing to high alkalinity, dissolved phosphate in interstitial solutions assumes the form of phosphate-carbonate complexes. Owing to the diffusion of CO_2 into near-bottom water, the alkalinity of the interstitial solution essentially drops while calcium phosphate falls out in interstices (Savenko, 1992).

Another mode of calcium phosphate deposition is governed by diagenetic phosphatization of organic remains, namely opaline and especially calcareous. The phosphatization of Recent foraminifera shells in

Table 1. Average chemical composition of sediments of the Namibian shelf (%)

Type of sediment	CaCO ₃	SiO ₂	C _{org}	Fe ₂ O ₃	MnO	TiO ₂	P ₂ O ₅
Terrigenous sediments	8.43	2.59	2.46	3.30	0.02	0.43	0.41
Calcareous sediments	60.49	0.50	3.55	1.39	0.01	0.17	1.69
Glauconitic sands	20.51	1.11	0.89	18.60	0.02	0.45	0.58
Slightly siliceous diatom oozes	9.24	19.75	7.01	3.03	0.01	0.37	0.50
Siliceous diatom oozes	4.49	39.9	5.35	1.31	0.01	0.01	0.82
Phosphatic sands	39.8	3.7	2.87	2.3	0.01	0.09	17.3

the Peruvian shelf sediments is described in detail by Manheim *et al.* (1975).

The variation of this process consists in the phosphatization of coprolites, which is important for rock formation, since many phosphatic grains and even larger nodules in these deposits originate from whole or fragmented coprolites belonging to zooplankton, fishes, or marine mammals (Baturin, 1978).

It is remarkable that the active phosphatization of coprolites in a Recent environment proceeds on the bottom surface, as evidenced by numerous findings in samples of diatomaceous oozes on the Namibian shelf. Even friable unlithified coprolites of sea lions contain no less than 25–27% P₂O₅ (Baturin, 1978), whereas coprolites in their natural state contain no more than 12–16% of this component (Hutchinson, 1950). Evidently, the organic matter of coprolites is highly reac-

tive and stimulates the phosphatization process, which proceeds very quickly, before coprolites are buried in sediments accumulated at the rate of about 1–2 mm/yr. The phosphorus needed for such a process may be supplied by near-bottom sea water or phosphorus-enriched pore water with its upward phosphorus diffusion.

Concentration of Phosphatic Material

The concentration of phosphatic material, initially dispersed in the source sediment, may take place owing to hydrodynamic activity driven by near-bottom currents or waves in shallow water during sea level changes.

As demonstrated by the phosphorite-bearing Namibian shelf, Recent diatomaceous oozes containing dispersed phosphatic material are neighboring reworked Pleistocene phosphatic sands (Fig. 6), which consist of analogous but concentrated material and differ only by the exclusively lithified nature of grains and nodules since unlithified material is destroyed during the reworking of original sediment. The latter has been similar in composition to Recent diatomatic ooze, as evidenced by diatom remains sealed in phosphatic grains and nodules (Baturin *et al.*, 1998a).

There is more evidence in favor of the genetic identity of Recent and Pleistocene phosphatic material and appropriate source sediments.

In particular, the P₂O₅ concentration in Recent diatom oozes is between 0.32 and 0.84%, whereas sand-sized material, whose share in bulk sediment is only 1.3 to 10%, contains 6–16% P₂O₅, predestining composition of relic sediments in the case of reworking (Baturin, 1978). According to a later, more detailed research, the chemical composition of individual sand fractions from Recent diatomaceous oozes is near to analogous fractions of Pleistocene sands; the same was observed when comparing nodules (Table 3).

A portion of the grains in phosphatic sands, as well as in diatom oozes, represents phosphatized coprolites; fine-grained and occasionally larger bone detritus is present in phosphatic sands (Bremner, 1978, 1992; Rogers, Bremner, 1991).

Table 2. Compositional evolution of Recent phosphorite nodules from the Namibian shelf in the course of their lithification

Components (%)	Slightly phosphatized diatomaceous ooze	Nonlithified nodule	Lithified nodule
P ₂ O ₅	7.49	23.28	32.41
CaO	12.6	35.6	48.7
MgO	1.62	1.48	1.51
Na ₂ O	3.47	2.89	1.16
K ₂ O	0.41	0.24	0.05
SiO ₂	37.8	13.0	0.2
Al ₂ O ₃	1.4	0.6	<0.02
Fe ₂ O ₃	0.58	0.30	0.09
TiO ₂	0.08	0.04	0.01
S ₂ O	0.10	0.24	0.30
BaO	0.09	0.14	0.07
CO ₂	2.96	4.94	6.36
C _{org}	3.97	1.41	0.87
S _{tot}	0.76	1.37	0.71
F	0.34	2.53	3.19

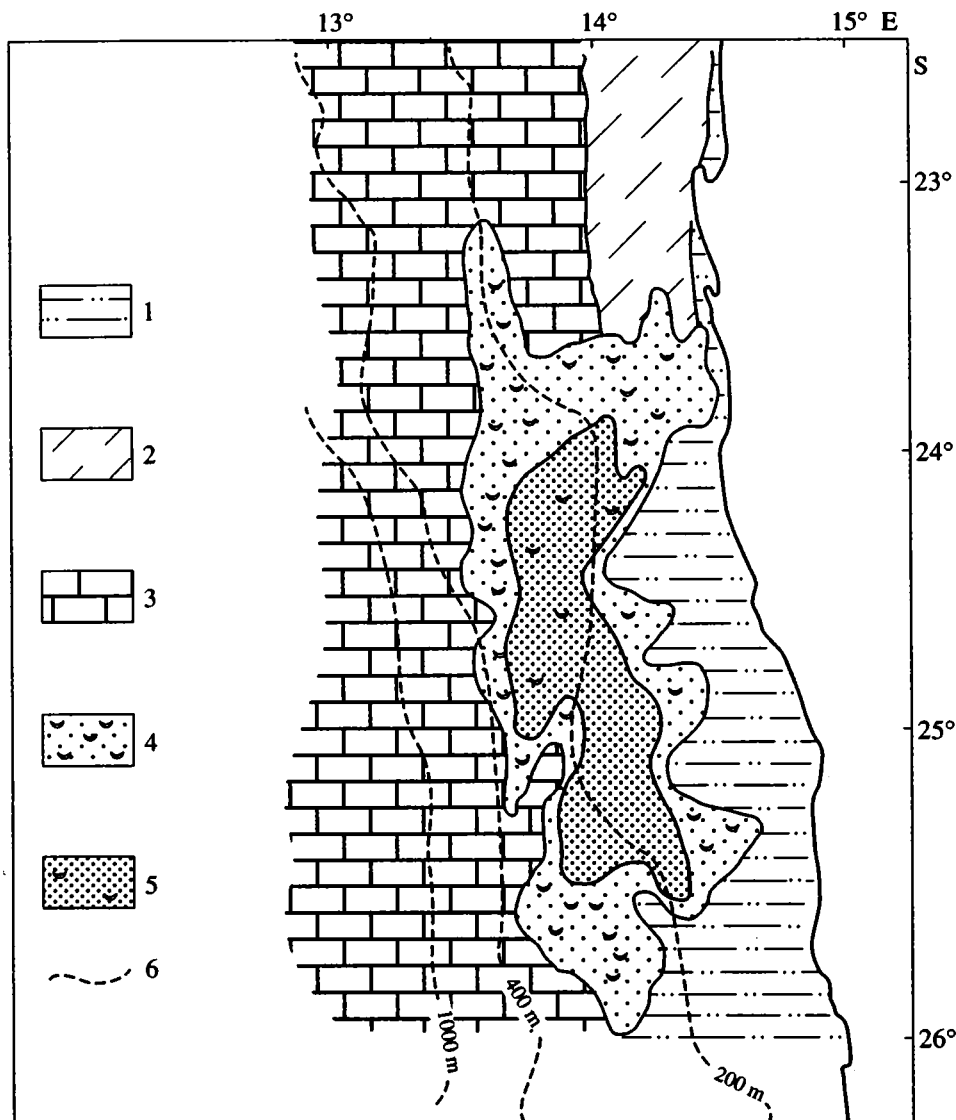


Fig. 6. Sediments of Namibian shelf, after Bremner (1978, 1992) and additional data of Emel'yanov (1973a, 1973b) and the author. (1) Terrigenous sediments; (2) diatomaceous oozes with dispersed phosphatic material; (3) calcareous, predominantly foraminiferal sediments; (4) shelly and phosphatic-shelly sands; (5) phosphatic sands with shell material; (6) isobaths.

COMPARISON OF HYPOTHESES TO RECENT PROCESSES

The above data demonstrate that Recent phosphate accumulation is not identical to either of the previous hypotheses. Nevertheless, the bulk of these hypotheses, especially the biogenic ones, previewed the essential features of the process. Let us try to make an appropriate comparison by discussing both previous and new hypotheses.

Biogenic Hypotheses

The most impressive in this aspect is the hypothesis of J. Murray and A. Renard (1891), which includes three basic conceptions: (1) the relation of phosphate

accumulation to water circulation from one side and to biological productivity from another; (2) the biogenic made of phosphorus deposition from sea water; (3) the diagenetic mechanism of phosphatic nodule formation.

The difference of this hypothesis from the Recent process consists of two points: first, it could not take into account the vertical water movement (upwelling), which was not well known at that time, and, second, it did not take into account the role of hydrodynamic activity as a factor of secondary or postsedimentary concentration of phosphatic material, which was highly stressed in later biogenic hypotheses.

A number of biogenic hypotheses, including the above, paid increased attention to bone detritus as a major source of phosphorite phosphorus which is

Table 3. Comparison of compositions of Recent and Pleistocene phosphatic nodules and grains from the Namibian shelf

Components (%)	Nodules		Grains					
	I	II	fraction 0.5–0.25 mm		fraction 0.25–0.1 mm		fraction 0.1–0.05 mm	
			I	II	I	II	I	II
P ₂ O ₅	32.41	30.74	25.45	10.91	29.46	25.50	30.40	25.77
CaO	48.7	49.1	40.55	25.7	49.50	44.1	51.36	45.7
MgO	1.51	0.93	–	1.39	–	1.22	–	1.12
Na ₂ O	1.16	0.45	2.22	0.92	1.88	1.26	1.90	0.98
K ₂ O	0.05	0.05	0.48	0.90	0.18	0.33	0.15	0.10
SiO ₂	0.2	1.7	8.96	39.9	3.64	6.20	2.18	4.7
Al ₂ O ₃	<0.02	0.5	0.98	2.6	0.22	1.2	0.25	1.1
Fe ₂ O ₃	0.09	1.6	0.57	4.8	0.37	3.9	0.57	3.1
TiO ₂	0.01	0.03	0.62	0.34	0.005	0.10	<0.005	0.08
SrO	0.30	0.30	0.33	0.14	0.39	0.26	0.39	0.27
BaO	0.07	0.04	–	0.01	–	0.02	–	0.05
CO ₂	6.36	4.86	1.06	8.78	1.46	6.03	1.23	7.06
C _{org}	0.87	1.42	3.90	1.05	3.43	1.30	3.50	1.43
S _{tot}	0.71	1.63	–	0.95	–	2.69	–	2.49
F	3.19	3.45	–	1.17	–	2.91	–	2.88

Note: Age of samples: (I) Recent, (II) Pleistocene. (–) no data.

mobilized in course of diagenesis and redeposited in the form of phosphatic nodules. The role of bone detritus was accounted for in later works as well (Baturin, 1978; Bremner, 1978; Suess, 1981; Rogers, Bremner, 1991; Föllmi, 1996).

Bone detritus in the Recent process accumulates in phosphatic sediments; however, its role as a phosphorus source for phosphatic grains and nodules is only secondary. Only a small part of bone material bears corrosion traces, which is usually accompanied by the phosphatization of these bones themselves (namely, their overgrowth and infilling by phosphate). Concurrently, phosphatic nodules contain bone fragments bearing no visible signs of alteration (Baturin *et al.*, 1970). Thus, the major source of phosphorus in the Recent process consists in planktonic, but not bone, detritus.

The next biogenic hypothesis, significant from a geological point of view, was suggested by Bushinskii (1963, 1966) and called "biochemical." It takes into account the biogenic source of phosphorus, the diagenetic mechanism of phosphatic components formation, and the hydrodynamic mechanism of their subsequent concentration. However, it postulates that river, rather than marine, water serves as a direct source of phosphorus in biogenic material and, subsequently, in phosphorites, which might predetermine an alleged spacial relation of phosphorites to mouths of some mythical phos-

phate-rich rivers. However, there are three arguments against this conception.

First, in spite of a highly variable geographical environment and large spectrum of rock composition of drainage areas, the concentration of dissolved phosphorus in river water does not exceed the background level of about 0.1 mg/l with the exception of rivers that are heavily polluted by anthropogenic dumping (Baturin, 1978; Meybeck, 1993; Savenko, Zakharova, 1995). Thus, there is no reason to suppose that phosphate-bearing rivers ever existed. Second, the concentration of phosphorus in river suspensions does not exceed its concentration in sedimentary rocks being on the average 0.06–0.07%. Third, the overwhelming part of suspended (up to 90%) and major part of dissolved material, including biogenic elements transported by rivers, is deposited on the river–sea boundary forming terrigenous sediments with the same background of phosphorus concentration (Baturin, 1978; Lisitsyn, 1978).

Finally, it is worth mentioning that all shelf areas of Recent and Late Quaternary phosphate accumulation are adjacent to arid continental areas and are not influenced by river runoff, owing to its nearly total absence.

Returning to the first coprogenic variety of biogenic hypothesis of Buckland (1829) that are it must be mentioned that his concept partially coincides with some of the Recent processes of phosphate accumulation. In particular, it was confirmed during the last century by the discovery of phosphatic guano deposits on islands

and sea shores of Peru, Chile, and South West Africa, located in the same biologically productive areas influenced by coastal upwelling, where Recent phosphorites were later found on the sea floor.

According to numerous investigations, abundant sea birds feeding on fishes and dwelling in these areas excrete daily from 30 to 120 g of guano, containing on average 4.3% P_2O_5 . The content of this component in Recent friable guano accumulated on the sea shore reaches 5.7–17.4%, increasing to 30.7–35.2% in leached and to 34.5–40.1% in lithified varieties.

The extent of this process is demonstrated by the following figures: in the Peru–Chilean region, guano accumulates on 147 islands and in 21 localities along the shore; some of these localities yielded 200–400 Kt of guano each in the period between 1916–1944. The rate of guano accumulation on Chincha Islands, which already yielded 11 Mt of guano, reaches 8 cm/yr (Hutchinson, 1950). On the Southwest African shore, guano is found in the band stretching from 22° to 35°S and even further to the North (up to 12°33' S) on some islands; its annual rate of accumulation in this area reaches 20 Kt (Hutchinson, 1950; Hart and Currie, 1960).

The total amount of phosphorus accumulating annually on sea shores near upwelling areas in form of guano excreted by fish-consuming birds reaches no less than 1–2 kt/yr. It is difficult to evaluate the amount of phosphorus settling to the bottom in the form of fish coprolites and marine animals. One might only suppose that the flux of coprogenic material makes a considerable share in the general balance of phosphate accumulation, since the annual fish production in coastal upwelling areas is evaluated as being 10 to 50 Mt (Marti and Parin, 1973). This consideration is supported by the fact that a portion of grains and nodules, in both Recent and many ancient phosphorites, is represented by phosphatized coprolites.

The microbiological variety of biogenic hypothesis attracts special attention.

It is largely known that bacteria are omnipresent and found in nearly all natural environments of the hypergenic zone, where they take part in metabolic processes. It is also known that some bacteria are able to concentrate phosphorus, although this amounts only to a small percentage (Hodson, 1977). However, the bacteria with specific phosphatic functions are unknown.

The primary argument by supporters of microbiological hypotheses consists in the findings of elongated and rounded micrometer-sized particles reminding bacterial and coccoidal forms in some phosphorites. However, the morphological similarity in this case is only a weak argument, since particles of the same size may fall out of interstitial waters oversaturated by calcium phosphate (Van Cappellen and Berner, 1991). Besides, the size of such particles varies greatly from less than 1 to 5–6 μm , that is not characteristic of the bacterial cells belonging to one and the same species (Steinier and

Edelberg, 1979). Elongated particles make up intergrowths and may form regular twins, trillings, rosettes, and stellar aggregates (Figs. 7a, 7b, 7c), which is typical in the mineral world. In cases where these particles are attached to hard surfaces, reduced forms appear with truncated bodies, similar to those observed during crystal growth. Moreover, many minerals, both natural and grown in laboratory experiments, including phosphates, sulfides, silica, and iron hydroxides, may form elongated and rounded particles of similar sizes (Baturin and Dubinchuk, 1979, 1989; Halbach *et al.*, 1988; Van Cappellen and Berner, 1991; Blake *et al.*, 1998).

Special investigations on the structure of Recent bacterial mats revealed that they contain only scarcely discernible bacterial remains, owing to the extremely fast lysis of bacterial cells under the action of ferments (Westall and Rince, 1994). Consequently, the excellent state of preservation and the abundance of assumed bacteria in some phosphorites, coupled with their total absence in the other parts of the same samples, is impossible to explain with microbiological hypotheses. More important is the fact that Recent oozes of the Namibian and Peru–Chilean shelves hosting Recent phosphatic nodules that are filled with such particles contain hydrogen sulfide associated with an abundant bacterial population, which is represented exclusively by filamentous sulfate-reducing bacteria without rods or coccoidal species (Butlin, 1949; Novozhilova and Baturin, 1973; Reimers *et al.*, 1990) (Fig. 7d).

Based on the above considerations, it is reasonable to interpret these particles as initial forms of phosphate deposition from interstitial solutions; some of these particles assume a crystalline appearance if enough free space is available. A number of other researchers engaged in the study of structure and composition of Namibian and Peru–Chilean phosphorites support this opinion (Burnett, 1977; Bremner, 1980; Garrison and Kastner, 1990).

The assumption that such particles have a bacterial nature may only prove that the bacteria are susceptible to phosphatization, along with any other organic substances, including those that are siliceous, calcareous, and especially carbonaceous (soft tissues, coprolites, wood, etc.). The same conclusion may be drawn from results of laboratory experiments with cyanobacteria, which are phosphatized when a dissolved concentration of phosphorus exceeds 15 mg/l (or nearly three orders of magnitude higher as compared to oceanic water) (Gerasimenko *et al.*, 1996).

It is symptomatic that numerous adherents of bacterial origin in phosphorites do not address the problem of systematics for their alleged bacterial findings, despite the fact that the modern scientific community is not lacking in experienced microbiologists who specialize in the oceanic bacterial population.

Concluding this section, it is reasonable to assume that the relation of phosphate accumulation to sediment

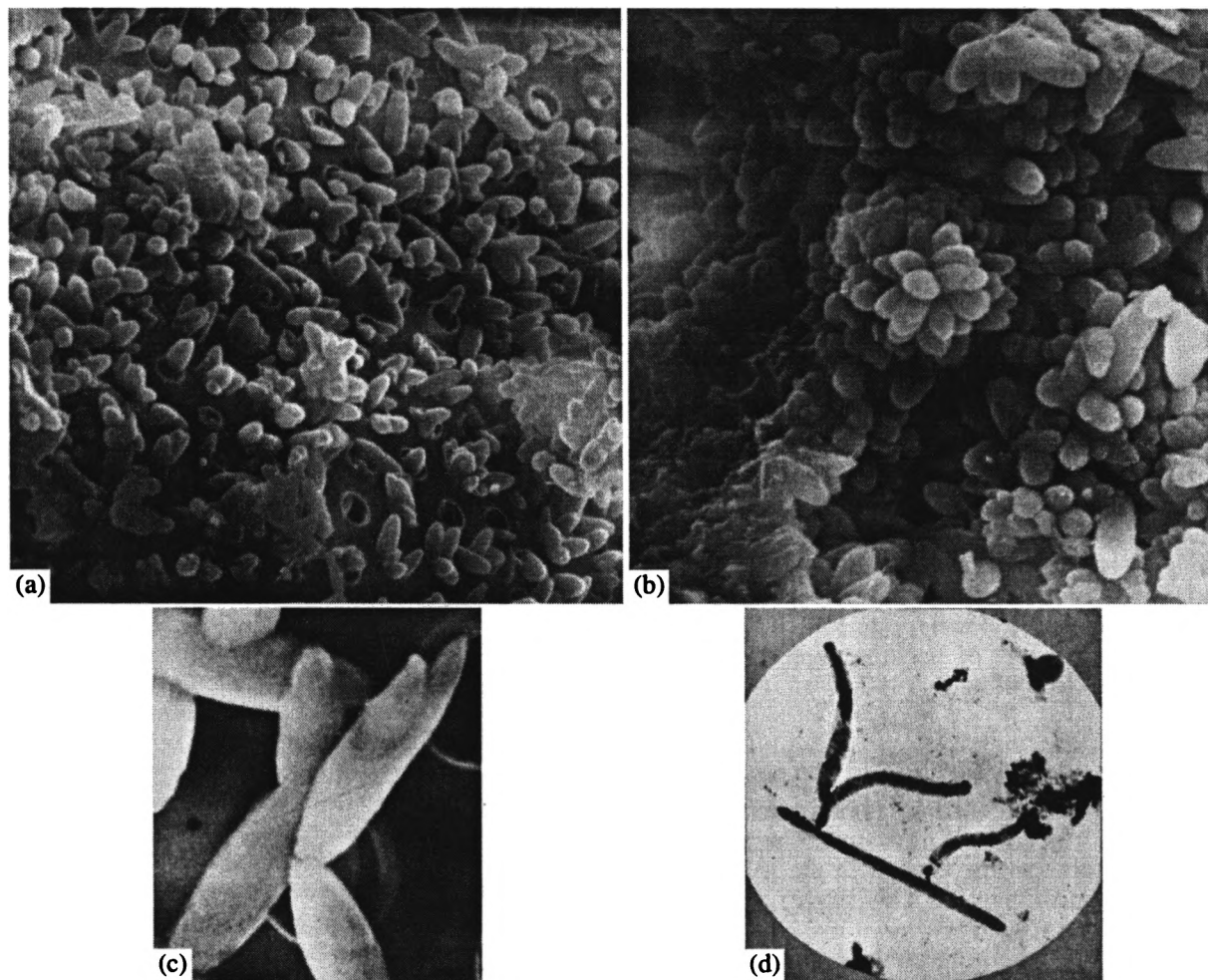


Fig. 7. Bacteria-like phosphatic crystallites in Recent nodules and sulfate-reducing bacteria from enclosing diatomaceous ooze on the Namibian shelf. (a) Accumulation of spindlelike crystallites on diatom frustule, magn. 7500; (b) aggregate of similar somewhat larger crystallites in the interstice, magn. 5000; (c) intergrowth of crystallites, magn. 20000; (d) filamentous sulfate-reducing bacteria from diatom ooze, magn. 7000 (Butlin, 1949).

red deposition, revealed by adherents of biogenic hypothesis, is sometimes criticized. In particular, Burnett *et al.* (1988) claims that the concentration of phosphatic pellets in unsorted sediments on the Peruvian shelf is evidence against the reworking of sediments. In opposition to this conclusion, other authors assume that the granulometric heterogeneity of phosphate-bearing sediments might be related to a number of secondary factors including postsedimentary bioturbation, storm action, and changes of the sedimentation regime in shallow areas (Garrison and Kastner, 1990).

It must be added that even thin-layered stratification of sediments does not mean the lack of water movement, which may induce the washing off of fine fractions. Freshly deposited ooze, especially diatomaceous ooze, represents a semiliquid substance, which might be suspended and washed off even by a slightly accelerated flow of water (Baturin, 1978; Rogers and Bremner, 1991) or owing to the accumulation of critical sed-

iment masses on steep bottom slopes. In such cases, the already consolidated phosphatic particles remain in place, i.e., on underlying denser sediments leaving no visible traces of reworking.

Chemogenic Hypotheses

When treating the chemogenic hypothesis of Kazakov (1939), it should be kept in mind that it is based on three assumptions: (1) the uneven distribution of phosphorus and carbonic acid in an oceanic water body (i.e., depletion in upper water layers and enrichment in deeper ones), (2) the upwelling of phosphorus- and CO_2 -enriched deep water onto shelf, and (3) the chemogenic deposition of calcium phosphate owing to its supersaturation in sea water. The first two points are inspired by oceanological data, whereas the third is relatively original.

The data concerning phosphorus distribution in Atlantic waters is taken from published materials of the German oceanographic expedition entitled *Meteor* (Wattenberg, 1927). As for upwelling, none of appropriate references are cited in Kazakov's publications, thus providing reason for the short review of the development of this problem.

According to oceanological history, initial information regarding cold water near the Peruvian coast was supplied by Augustin de Zarate in his report to the king of Spain in 1555. English sailors of the 16th century F. Dreik and D. Haukins also knew about the cold current near the Peruvian coast. In 1802, this phenomenon was observed by A. Humboldt, who related it to a northern extension of the cold Antarctic current. However, as early as 1844, the French investigator U. de Tesson supposed its local origin. The same was supposed by the English captain J. Ross, who discovered cold water near the Southwest African coast in 1847. Later, by the end of the 19th century, a series of theoretical investigations by German investigators appeared, explaining the coastal upwelling phenomenon by the interaction of wind and hydrophysical fields coupled with Earth's rotation forces (A. Buchan, E. Witte, P. Hoffman, and others).

At the beginning of the 20th century, after a series of oceanographic expeditions, it was unequivocally shown that cold water is, in fact, local and is upwelled from a relatively shallow depth of about 100 to 250 m (A. Defant, G. Dietrich, H. Sverdrup, A. Franz, G. Schott, and others).

However, when building his hypothesis, Kazakov ignored these data and arbitrarily "lowered" upwellings to be as deep as 1000 m, where the phosphorus concentration is somewhat higher. In this assumption, he did himself a disservice, since it motivated many geologists to reject his model as inadequate hypothesis for shallow phosphorite-bearing basins with limited relation to open ocean (Bushinskii, 1966; Librovitch, 1966).

The main idea of Kazakov's hypothesis, namely, the direct deposition of calcium phosphate from marine and oceanic waters, is based on experiments run under conditions far from natural concerning all basic parameters including solution composition, phosphorus speciation, and others. However, even more important is the fact that chemogenic phosphate deposition was never observed in any of Recent basins despite a large variation in their hydrochemical regimes and enormous amount of hydrochemical observations accumulated during more than 60 years since Kasakov's first hypothesis.

The most essential property of phosphorus governing its behavior in hypergenic zone is its biophylic nature, which is greatly restricts the role of purely chemical processes.

The average C/P ratio in oceanic phytoplankton is 40 (the Redfield ratio) whereas its carbon production reaches 50 Gt (Romankevitch *et al.*, 1998). Conse-

quently, the annual rate of phosphorus consumption, by oceanic phytoplankton is nearly 1.2 Gt, whereas the amount of dissolved phosphorus in the photic zone inhabited by phytoplankton, is estimated as being 0.5 Gt. It means that all phosphorus contained in the upper layers of oceanic water participates in biogenic cycle several times yearly, leaving no place for its purely chemical deposition. The study of oceanic suspensions by means of sediment traps proved that the deposition of biogenic elements, including phosphorus, from sea water proceeds exclusively through pelletal transport; i.e., it is incorporated into biogenic particles. In most fertile sea waters, especially in coastal waters off Peru, Chile, and southwestern Africa, the daily production rate of organic detritus reaches 6 to 9 g/m², of which a certain part reaches sea bottom (Lisitsyn and Vinogradov, 1983). This process is clearly seen when comparing the schemes of phosphorus and biological productivity distribution in coastal southwestern Africa waters, with appropriate distribution schemes of phosphorus and organic matter in underlying sediments (Figs. 8, 9). These schemes demonstrate that dissolved phosphorus nourishes biological productivity, whereas the latter controls the distribution of organic matter and phosphorus in sediments.

The results of recent experimental works show that oceanic water, with an average phosphorus concentration of about 70 µg/l (the maximum being up to 100 µg/l), is at least one order of magnitude undersaturated relative to calcium phosphate (Savenko, 1992); its deposition occurring in the form of gel requires a long period of time in stable laboratory conditions, not comparable with the open ocean environment.

The only observed chemogenic process, which actually induces phosphorus extraction from Recent oceanic waters, consists in its coprecipitation with ferric suspensions supplied to a water body by high-temperature hydrothermal solutions from rift zones (Feely *et al.*, 1990). However, this mechanism plays only a minor role in the general balance of phosphorus, as compared to prevailing biogenic sedimentation.

The metasomatic variety of chemogenic models (Ames, 1959) consisting of carbonate phosphatization in the course of its contact with sea water equally meets no direct proof in Recent ocean. Findings of phosphatized carbonates on the oceanic bottom are numerous, however, it is unclear whether phosphatization occurred above or below the bottom, i.e., owing to contact with marine or interstitial waters.

The metasomatic variety of the hypothesis of hydrogen sulfide phosphogenic basins or the hydrogen sulfide-biogenic model uses the Black Sea and other hydrogen sulfide-infected basins as an example, attempting to apply its environment to phosphorites of the Karatau and other phosphorite deposits of similar geological settings (Kholodov and Paul, 1995a, 1995b, 1996; Kholodov, 1997). This hypothesis has its own historical background.

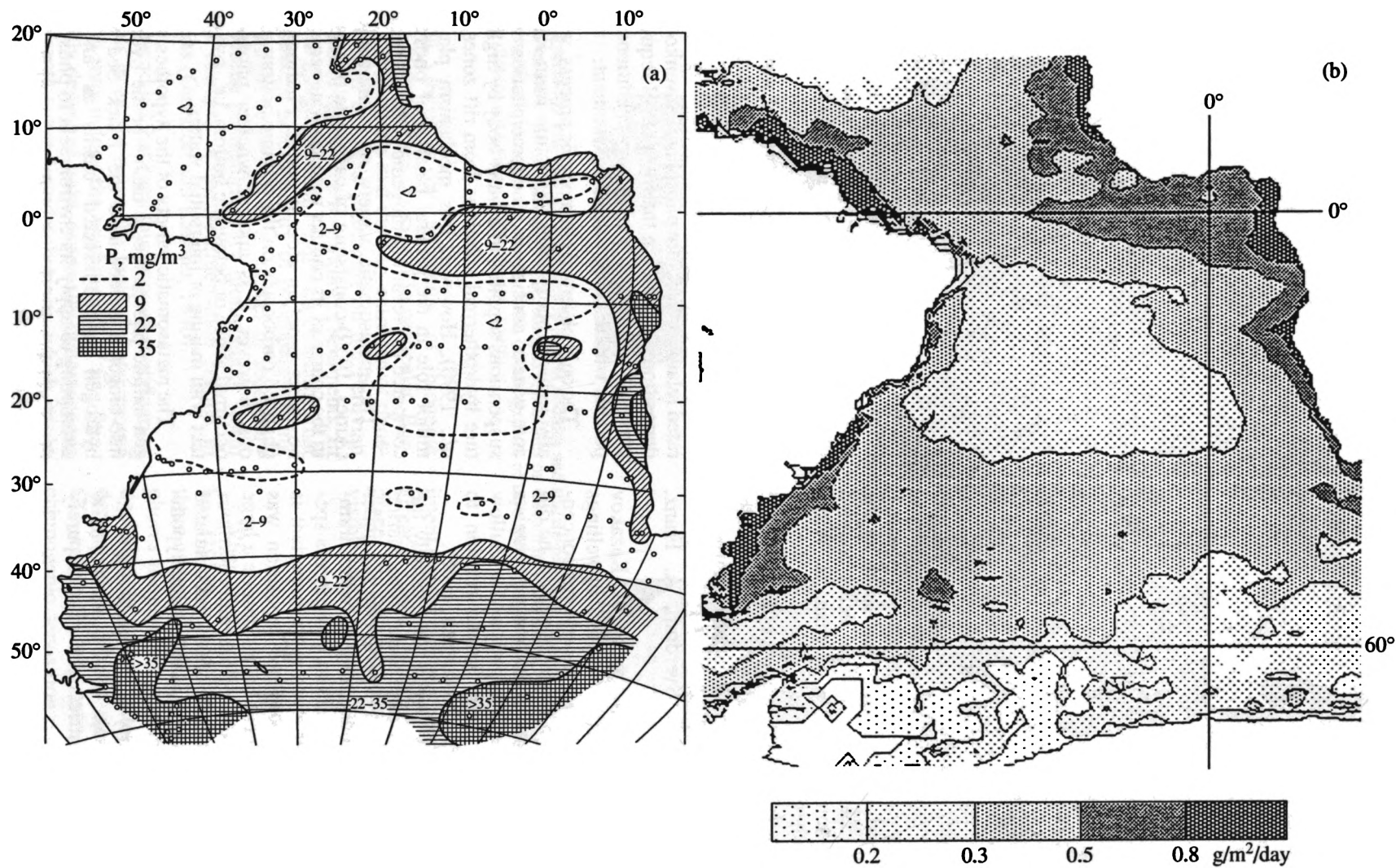


Fig. 8. Distribution of dissolved phosphorus and primary biological production of phytoplankton in surface waters of the Southern Atlantic. (a) Dissolved phosphorus, mg/m^3 (Wattenberg, 1927); (b) primary production, $\text{g/m}^2/\text{day}$ (Vinogradov *et al.*, 1996).

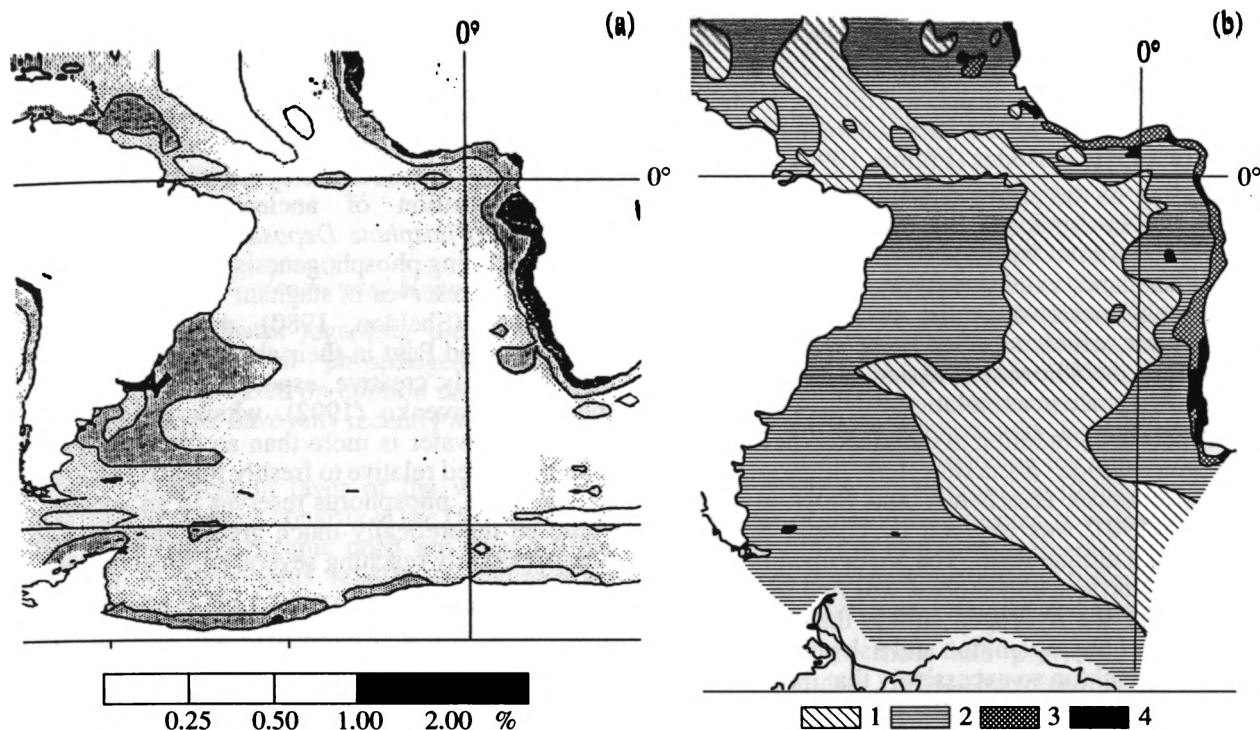


Fig. 9. Distribution of organic carbon and total phosphorus in the surface sediment layer of Southern Atlantic. (a) Distribution of C_{org} (Romankevich *et al.*, 1998); (b) distribution of phosphorus, in % (Emel'yanov and Romankevich, 1979). (1) <0.05; (2) 0.05–0.1; (3) 0.1–0.2; (4) >0.2.

Some authors suggest that ancient phosphorites of India and China were formed by stromatolith phosphatization owing to their contact with anoxic waters of the Proterozoic Ocean which is enriched in phosphorus and carbonic acid (Banerjee, 1978; Sheldon, 1980).

From another perspective, a number of scientists came to the conclusion that phosphate accumulation in Phanerozoic basins is related to transgressions and sea level rises (Fisher and Arthur, 1977; Cook and McElhinny, 1979; Arthur and Jenkins, 1981; Glenn *et al.*, 1994), which can lead to a lack of vertical circulation, inducing oxygen deficiency, or its total absence coupled with the accumulation of dissolved phosphorous in deep waters (Sheldon, 1980; Kennett, 1987).

Another supposition is that phosphorites on the submerged mountains of the Pacific were formed by the metasomatic phosphatization of limestones, washed by phosphorus-enriched waters during episodes of oceanic anoxia (Hein *et al.*, 1993). However, it seems that only the Maikop sea, where deposits of bone breccia formed on its shelf, may be considered as a reliable example in the association of phosphate accumulation with hydrogen sulfide-infected water bodies (Kochenov and Stol'yarov, 1996).

It is of interest to note that phosphatization of various phosphatic materials in dissolved phosphorus-enriched anoxic media has been repeatedly modelled in experiments. The first attempt to phosphatize corals

and crustacean coprolites was made before the end of the 18th century (Murray and Irvin, 1889; Irvin and Anderson, 1891). During recent years, a series of experimental phosphatization of biogenic carbonates in phosphorus-enriched marine and fresh water were completed by French investigators (Lucas and Prévôt, 1984a, 1984b, 1985).

It may seem that these results provide evidence in favor of the alleged genetic relation between hydrogen sulfide-infected basins and phosphate accumulation, however, there may be some arguments opposing this idea.

In most cases, episodes of anoxia in Phanerozoic oceans and phosphate accumulation in their periphery, did not coincide in time and space (Kennett, 1987; Föllmi *et al.*, 1993; Lucas, Prévôt, 1995). If one takes into account that the mixing time of oceanic water does not exceed 1000 yr, whereas the residence time of phosphorus in the ocean is only one order of magnitude greater (Ruttenberg, 1993), the genetic relation between discussed phenomena would seem not realistic.

The attempt to relate phosphate accumulation in the submerged mountains of the Pacific to anoxia in intermediate layers of a water body (Hein *et al.*, 1993) seems unconvincing in light of lithological and geochemical observations revealing the extremely patchy nature of phosphatization evidently related to diagenetic processes (Gaioty ..., 1995).

It has been established that anoxic episodes during the last 160 Ma did not reduce the supply rate of both total and organic phosphorus to sediments of the world ocean. It may mean that phosphorus did not accumulate here owing possibly to the local character and short duration of anoxic episodes (Föllmi, 1996).

According to the above considerations, phosphate accumulation in Cretaceous basins proceeded without any direct relation to hydrogen sulfide contamination. On the other hand, extensive hydrogen sulfide expansion embracing nearly the entire water body, including its photic layer, which occurred in the eastern Mediterranean during the Pliocene (Passier *et al.*, 1998), produced no phosphate accumulation.

Phosphate accumulation in the Maikop basin, where a hydrogen sulfide excursion left lithological and geochemical traces (Kochenov and Stolyarov, 1996; Nedumov, 1998), was induced by coastal upwelling and assumed a unique form. The water upwelled to the Eastern and Northeastern shelves was rich in phosphorus but free of the hydrogen sulfide that flavored the development of phytoplankton and fish population. The latter fed on plankton so excessively that the accumulation of planktonic sediments were extremely reduced as well as the whole diagenetic phosphorite formation stage. As a result, phosphatic material accumulated as biogenic fish remains, with only a minor amount of diagenetic phosphorite nodules (Mstislavskii and Kochenov, 1960; Kochenov and Stolyarov, 1996).

The most typical among Recent hydrogen sulfide basins is the Black Sea, whose deep waters are three times more concentrated in phosphorus when compared to the ocean; however, neither phosphate accumulation nor carbonate phosphatization occurs in its sediments, whereas phosphorus concentration in coccolith oozes exposed on its bottom is usually below 0.1% (Glagoleva, 1959). Calcareous and other shelf sediments situated near to or above the hydrogen sulfide boundary equally reveal no signs of phosphatization.

On the other side, in areas where Recent phosphorite-producing sediments accumulate on the Namibian and Peru–Chilean shelves, hydrogen sulfide appears in near-bottom water only sporadically, owing to its diffusion from organic-rich sediments. This might be considered as only one of the many phenomena accompanying phosphate accumulation.

Lastly, the results of above experiments, forcing the metasomatic phosphatization of organic materials in solutions enriched in phosphate to be several orders of magnitude greater as compared to natural marine environment, imitate a diagenetic rather than sedimentary situation.

These considerations highlight at least two moments: first, phosphatic sediments do not accumulate in Recent hydrogen sulfide basins; second, Recent phosphatic accumulations do not directly depend on sporadic hydrogen sulfide excursions in bottom water

taking place mainly during the normal aeration of a water body.

Nevertheless, it is likely that the gas regime, hydrochemistry, and sedimentation conditions in Cambrian and Precambrian basins could be much different from Recent ones, as evidenced by peculiarities of structure and composition of ancient phosphorite-bearing sequences (*Phosphate Deposits ...*, 1986). Therefore, the idea relating phosphogenesis to the accumulation of phosphorus reserves in stagnant waters of a transgressive ocean (Sheldon, 1980), developed further by Kholodov and Paul in their above-cited work, may be seen as highly creative, especially in light of experiments by Savenko (1992), which demonstrate that Recent sea water is more than an order of magnitude undersaturated relative to freshly formed calcium phosphate; hence, phosphorus reserves in an ancient ocean could be theoretically much greater than in a Recent ocean, possibly reaching several trillions of tons.

Hypothesis of the Phosphatic Pump Trap

The hypothesis of the phosphatic pump trap (Froelich *et al.*, 1988) has been suggested to explain the discrepancy between a high phosphate/ammonia ratio in pore water and the deficiency of phosphorus-bearing organic matter in surface sediments of the Peruvian shelf. The authors of this hypothesis related excess phosphorus in pore waters to dissolution of bone material, which was previously suggested by Suess (1981). However, abundant phosphorus-rich pelletal and coprogenic material seems to be a much more important source of this excess phosphorus. According to our observations, only a minor part of small pellets present in Recent sediments is endured, whereas their greater part is subject to quick disintegration. It is possible that phosphorus released from pellets is enriching pore water of the upper sedimentary layer; this consideration is strengthened by observations of Porter and Robbins (1981) who found that up to 50% of phosphorus contained in some ancient black shales is bound to coprogenic pellets.

Moreover, the hypothesis of phosphatic pump trap is hardly applicable to phosphate-bearing diatomaceous oozes of the Namibian shelf for two reasons: first, the oxidation–reduction boundary in this area is usually above the bottom surface; second, these oozes are very poor in iron (below 1% Fe), which is bound to pyrite and, hence, is immobilized.

As for the convection-diffusion hypothesis assuming phosphorus pumping from bottom water into a sediment (Föllmi and Garrison, 1991), it is based exclusively on theoretic considerations. According to actual observations, the concentration of phosphorus in pore waters is constantly higher than in bottom waters, inducing its upward rather than downward flux (Baturin, 1978; Savenko, 1992; Bogdanovskaya, 1993).

It seems more probable that the origin of phosphatic crusts and phosphatized hardgrounds is better explained by Jarvis (1980), who related the phosphatization of hard surfaces to their colonization by bottom fauna and the development of algal mats, i.e., to the combination of biogeochemical and diagenetic processes.

Volcanogenic-Hydrothermal Hypotheses

Long-standing debates regarding the problem of volcanogenic-hydrothermal phosphogenesis, which were often primarily based on opinion rather than factual experimentation, have only recently acquired more distinct features.

A major argument in favor of the volcanogenic-hydrothermal hypothesis consists in the fact that basaltic rocks forming the oceanic crust are three to four times richer in phosphorus relative to sedimentary rocks containing only 0.06-0.07% P on the average. This was thought to be adequate in solving the problem of the ocean's phosphorus source, especially in view of the apparent phosphorus depletion in weathered oceanic basalts (Kurnosov, 1986).

However, even the first experiments modeling the interaction of powdered basalt with heated marine water under high pressure revealed that phosphorus is poorly soluble in contrast to iron and manganese: its maximum concentration in an artificial hydrothermal solution at 400°C reached only 0.4 mg/l (Mottle *et al.*, 1974). If hot basalts of oceanic rift zones annually contact 200 to 490 km³ of sea water (Lisitsyn, 1983), the assumed yield of such conventionally endogenic phosphorus would reach no more than 100 kt, which makes less than 1% as compared to riverine supply. Moreover, not all of this phosphorus may reach the oceanic water body, since part of it is bound to iron oxide crusts covering surfaces of weathered basalts (Hart, 1970).

Even more impressive results have been obtained during investigations of high temperature (350–400°C) hydrothermal solutions sampled close to active vents: their phosphorus concentrations resulted as being even lower than in oceanic bottom waters (Tunnicliff *et al.*, 1986; Gordeev, 1992).

High phosphorus levels occasionally exceeding 1 mg/l, which are sometimes found in thermal postvolcanic waters of the Kamchatka and some volcanic islands (Baturin, 1978), are evidently related to the drainage of volcanic ashes containing relatively mobile phosphorus. However, such a situation is far from that, which is typical for oceanic rift areas, where hydrothermal solutions percolate through crevices in fresh basalts. Aside from this, dry residue of hydrothermal solutions, as well as sinters, is generally poor in phosphorus, whose concentration does not exceed 1%.

The problem of assumed volcanogenic origin of phosphorites in submerged islands of the Pacific has also been subject to much discussion. The light isotopic

composition of phosphate-bound oxygen in some of these samples has been interpreted as unequivocal evidence of the high temperature appropriate for mineral-forming solutions (Strizhov *et al.*, 1985; Hein *et al.*, 1993).

However, it was established that phosphate-bound oxygen is liable to isotopic exchange with surrounding waters at high temperature and pressure, which has been clearly demonstrated by phosphorites of the Monterey Formation as an example (Kastner *et al.*, 1990). Therefore, sporadic anomalies contrasting to generally normal background isotopic oxygen composition of phosphorites in submerged mountains might be related to their contact with heated postvolcanic hydrothermal solutions inducing the appropriate isotopic shift (Baturin and Pokrovskii, 1998). The sedimentary origin of these phosphorites is well confirmed by the composition of rare earth elements, which are similar to those of oceanic waters and differ from those of hydrothermal solutions (Baturin and Yushina, 1998).

According to these and previous data (Baturin, 1978; *Concepts ...*, 1994), the volcanogenic-hydrothermal process is inadequate in the ability to form directly a considerable phosphorite deposit either in Recent or in ancient basins. Nevertheless, it might be accepted that the weathering of volcanogenic and hydrothermal materials, in particular ash and volcanoclastics on land and in sea during epochs of active volcanism in the Earth's history, could supply a considerable amount of mobile phosphorous to the ocean. However, the migration of such alleged volcanogenic phosphorous through long distances in a marine environment, according to Shatskii (1955), seems quite unrealistic owing to immediate involving of phosphate supplied to the sea into biogeochemical turnover. The most detailed and convincing geological and geochemical data demonstrating a lack of any relation of phosphate accumulation to volcanic and hydrothermal processes during the Earth's history was recently presented by Kholodov and Butuzova (1999).

Endo-upwelling Hypothesis

The endo-upwelling hypothesis of Rougerie and Wauthy (1986), which is similar to some extent to the former model by Corliss (1971) in assuming the infiltration of sea water into hard rocks and its transformation into an ore-bearing solution, appears alternative to the oritogenic hypothesis of phosphorite formation on oceanic islands and atolls (Hutchinson, 1950). However, Corliss' hypothesis has been subsequently supported by the discovery of *black smokers*, whereas endo-upwelling is questionable. According to the first variety of this hypothesis (Rougerie and Wauthy, 1986, 1993), oceanic water with a moderate phosphorus concentration (0.04 mg/l) moves upward through limestone deposits about 800 m thick and reaches a shallow brackish lake situated on the atoll surface, where cal-

cium phosphate chemically precipitates. No proof of such a process has been offered.

According to the next variety of this hypothesis (Jehl and Rougerie, 1995), phosphate dissolved in lake waters is extracted by bacterial mat with an average P concentration of 0.1%. It is supposed that the growth of bacterial mats alternates with dry periods, when they are totally destroyed, leaving a residual calcium phosphate, which is subject to subsequently repeated redeposition yielding rock with 40–47% P_2O_5 .

Finally, one ton of bacterial mat is thought to produce 2–3 kg of high-grade apatite similar to that found on some ancient atolls.

It seems that the above model ought to be supported by finding the lacking stage of this succession that binds 0.1% P in bacterial mats on some Recent atolls to high-grade apatite with 40–47% P_2O_5 on ancient ones.

CONCLUSION

The present review deals only with some aspects of phosphogenesis including the most important which is formulated as the possibility of comparing Recent processes with those pertaining to a geologic past.

In his time, Bendor (1980) gave a negative answer to this question; however, later investigations demonstrated that such a comparison is justified owing to three reasons. First, much of the phosphorite deposits formed in shelfal biologically productive areas influenced by coastal upwelling; second, phosphatic material of such deposits consists of grains, nodules, phosphatized coprolites, and bone detritus comparable in their morphology and composition to those characteristic for Recent phosphate accumulations; third, concentration of this material occurred owing to the reworking of sediment.

No less remarkable is the fact that the rate of Recent and Late Quaternary phosphate accumulation is comparable to formation rates of the largest Miocene and Cretaceous phosphorite deposits (Baturin, 1978; Filipelli and Delaney, 1992; Baturin *et al.*, 1995).

Owing to the discovery of a number of new deposits, the idea of a limited number of so-called phosphogenic epochs needs reevaluation, since the age range of phosphogenic processes was found to be much larger than it previously seemed (Cook and McElhinny, 1979; *Concepts ...*, 1994; Föllmi, 1996). Time needed for the formation of a large phosphorite deposit is estimated as being several million years, whereas the duration of nonphosphatic epochs remains much longer, as compared to phosphatic ones, including the Recent.

The Recent oceanic environment is comparable, in its paleogeographic aspect, to interglacials in general. Since the formation of diagenetic apatite in sediments of continental margins is, according to recent data, a global and permanent phenomenon (Ruttenberg and Berner, 1993), the concentration of phosphatic material into a deposit is possible owing to the optimal coinci-

dence of active biogenic sedimentation on a shallow shelf, stable tectonic regime, and the microfluctuations of sea level, providing a repeated change of sediment accumulation and reworking. Such a mechanism seems more realistic than the assumed anomalously fast short-time phosphorus supply to the ocean.

One more important aspect of phosphogenesis consists in how much of it is dependant on upwelling. Owing to an incorrect interpretation of the upwelling phenomenon by Kazakov, many geologists unfamiliar with oceanographic information still imagine that the upwelling mechanism works only in the deep basins of oceanic type. In fact, upwelling in water basins is as common as wind in the atmosphere and does not depend on basin depth driving upward the phosphorus-enriched water needed to support biological productivity of the upper water body. Therefore, there is no ground to suppose that upwelling did not occur in ancient shallow basins.

However, several findings of low-phosphorus nodules on the eastern Australian continental slope in an area of weak sporadic upwelling, provoked the question of whether upwelling is necessary for phosphate accumulation at all (O'Brian and Veeh, 1983). It seems that the answer consists in a character of such findings themselves: weak upwelling produces poor phosphorites.

One more acute problem concerns the role of microorganisms in phosphate accumulation. It is evident that the degradation of organic matter and the mobilization of associated phosphorus is impossible without microbial action. A number of experiments proved, as well, that bacteria greatly accelerate the deposition of calcium phosphate from a solution (Lucas and Prévôt, 1984a, 1984b, 1985), which might be related to the catalytic action of bacterial enzymes. However, until recently, there was no evidence of the direct relation of phosphorus concentration in sediments to any specific function of certain microorganisms, if at all. To settle this problem, additional integrated efforts are required from geologists, geochemists, and microbiologists, including, first of all, specialized microbiological investigations of the sea in areas of Recent phosphorite formation.

Lastly, the problem of an assumed relation of phosphate accumulation to hydrogen sulfide basins (Kholodov and Paul, 1995a, 1995b, 1996; Kholodov, 1997) would raise further discussion bearing in mind that the ground for estimation of this idea was paved long ago by Sheldon (1980), who theorized that phosphorus accumulated in stagnant waters during high sea level stands may serve as a reserve for subsequent phosphate accumulation realized through the mechanism of equatorial upwelling.

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Genetic Characteristics of Sands in the Northeastern Gulf of Finland: Evidence from Grain-Size Distribution

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Abstract—Results of the analysis of grain-size distribution in 21 fractions of sands from the northeastern Gulf of Finland are discussed. A method of cumulative curves is proposed for the lithofacial analysis of sands. Cumulative curves are divided into four major types and several subtypes corresponding to specific dimension, sorting grade, and position in the bathymetric profile. The relationship between curve types and modern hydrodynamic conditions is examined. The method promotes a more efficient application of genetic criteria for lithological mapping and can be used for paleodynamic reconstructions.

The analysis of sedimentation conditions on the basis of grain-size composition is an important aspect of sedimentology. The analysis can be carried out by various methods. Methods based on statistical parameters such as median, standard deviation, and asymmetry, which possess certain physical and sedimentological significances (Folk and Ward, 1957; MacLaren and Bowles, 1985; Rozhkov, 1978; and others), use genetic diagrams (Friedman, 1961; Passega, 1964; Rukhin, 1969; Stapor and Tanner, 1975; and others). Graphical methods based on the analysis of grain-size composition of sediments as a whole use histograms, distribution curves (Kotelnikov, 1989; Usenkov and Barkov, 1995), and cumulative curves (Visser, 1969).

It should be noted that the knowledge of data on grain-size distribution, i.e., the number of grains in each fraction, is an essential condition required for the correct estimation of grain-size statistics. Existing methods for the recalculation of weight percentage into number of grains are inadequate for the analysis of polyfractional sands (Romanovskii, 1988). Publications devoted to this problem indicate that poor reproducibility is an additional shortcoming of methods based on grain-size distribution.

The implication of the cumulative curve method for the genetic interpretation of sediments was scrutinized in the 1930s–1950s (Doeglas, 1946; Van Andel and Postma, 1954; Visser, 1969). These researchers identified several types of the probability-scale cumulative curve and revealed a correlation between the curve type and specific hydrodynamic constraints of sedimentation.

The cumulative curve method was criticized by several researchers during a discussion on the correspondence of grain-size distribution to the lognormal model (Bagnold and Barndorff-Nielsen, 1980; Grace *et al.*, 1978; and Romanovskii, 1988). However, experimental

works (Sagoe and Visser, 1977) and detailed studies (Bridge, 1981; Middleton, 1976; and others) demonstrated the validity of this method and the possibility of its application for the dynamic and facies analysis. Currently, this method is widely used by researchers in Russia and abroad for the analysis of grain-size distribution of clastic sediments and the elucidation of their genetic criteria (Gurevich and Kazakov, 1981; Kennedy *et al.*, 1981; Lider, 1986; Rybalko, 1973; and Tauber, 1997).

This work is based on the grain-size distribution of 229 samples of beach sand from the northeastern Gulf of Finland. We tested various methods of the grain-size analysis. The genetic diagram method, which was successfully used by other researchers to identify dune, river, and marine sands, was unsuitable for our samples. The distribution curve method, which is essential for analysis of the grain-size composition of sediments, was also inappropriate, because distribution curves are more strongly governed by individual features of grains relative to cumulative curves. Therefore, we chose the probability-scale version of the cumulative curve method as the main tool for studying the impact of sedimentational environment on the sediment and its reworking grade.

The analysis of cumulative curves has made it possible to divide them into four major types representing specific hydrodynamic conditions and submarine topographic features. The possibility of computer database processing makes the cumulative curve method simple and vivid. Therefore, in combination with conventional granulometric coefficients and distribution curves, which are used for deciphering the unimodal or bimodal nature of sediments, this method can be applied for solving the problem of genesis of coastal-marine sands.

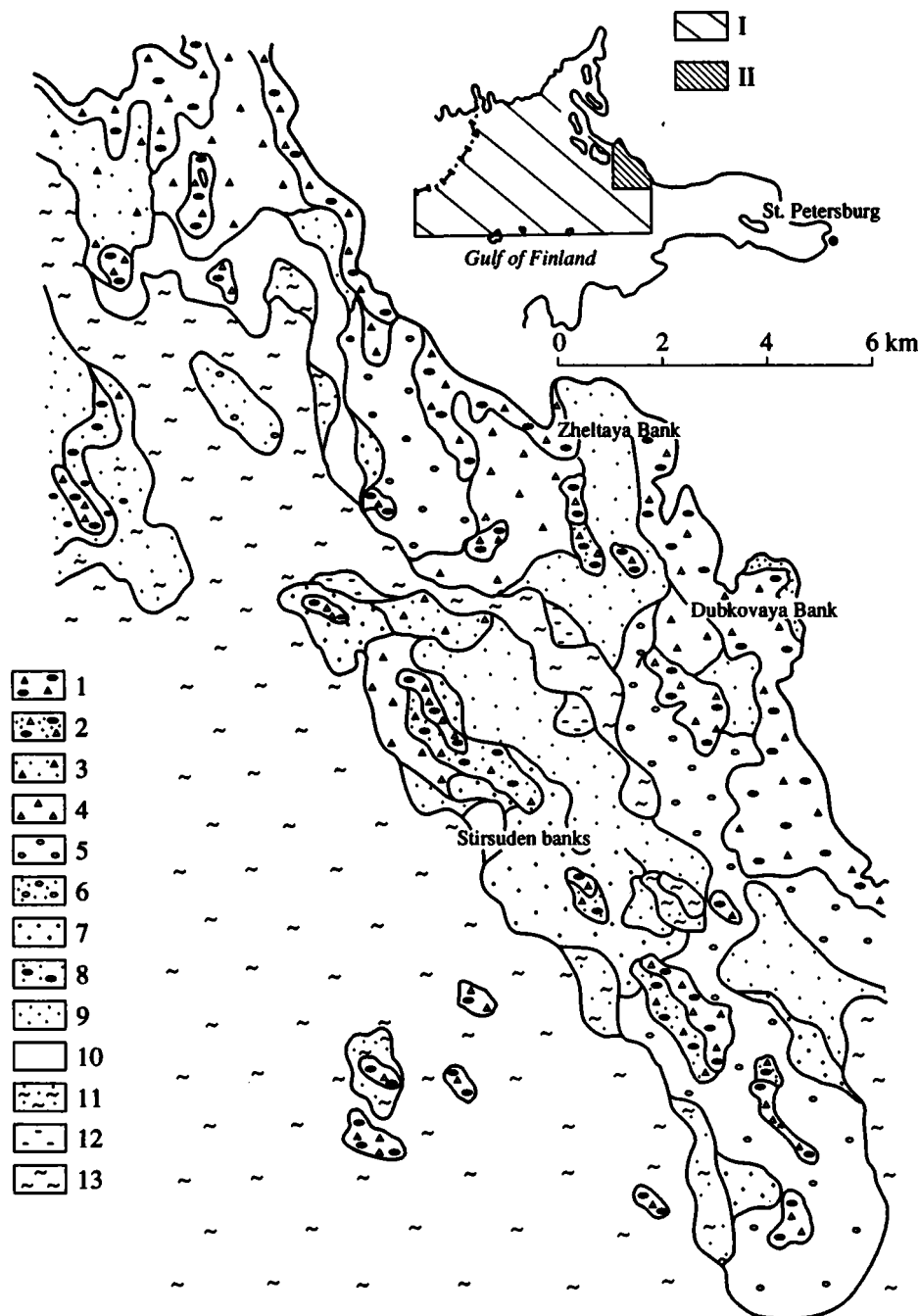


Fig. 1. Schematic lithological map of surficial sediments in the northeastern Gulf of Finland (the southeastern area of Berezovye Islands). (I) Sampling area; (II) the southeastern area of Berezovye Islands. Sediment types: (1) gravel, pebble, and sand; (2) gravelly; (3) inequigranular, mainly coarse-grained; (4) coarse-grained and large- to coarse-grained; (5) medium- and coarse-grained; (6) inequigranular, mainly medium- and coarse-grained; (7) medium-grained and fine- to medium-grained; (8) inequigranular, mainly fine- and small-grained; (9) small-grained and fine- to small-grained; (10) fine-grained and small- to fine-grained; (11) silty and clayey sands; (12) silt; (13) clay and silty clay.

GEOLOGICAL-GEOGRAPHIC AND HYDRODYNAMIC CONSTRAINTS OF SEDIMENTATION

The data used in this work were collected during the experimental-methodological study, geological survey,

and prospecting in 1980–1993 by researchers from the Regional Geoecology and Marine Geology Division, VSEGEI. The study region is located between the Moshchnyi, Malyi, Zapadnyi Berezovyi, and Sommers islands in the northeastern Gulf of Finland (Fig. 1).

Depth intervals within the region are as follows (from east to west): 20–40 m near the Seskar Island area, 40–50 m up to Moshchnyi Island, and as much as 70 m in the western Moshchnyi Island area. The bottom topography is strongly dissected (Moskalenko, 1989). The mouth of Vyborg Bay and the northern shoal zone include numerous skerry-type islands. The northern sector incorporates several submarine, mainly NW-oriented, extended ridges with depths of less than 20 m. The eastern area of the Bol'shoi Berezovyi Island hosts a series of SE-oriented ridges (at depths of 5–10 m) that are separated by narrow ravines with steep slopes and are characterized by relative topographical variations up to 10–20 m. The flat ravine floor gently dips toward the southeast and reaches a depth of 30 m.

The hydrodynamic regime, which is responsible for several features of the distribution, accumulation, washout, and lithodynamics of sediments in the northeastern Gulf of Finland, is mainly controlled by synoptic factors. The intense air regime in this region is primarily related to Atlantic cyclones. The number of stormy days is 40–50 per year. The wave height can reach 3 m in the open part of the Gulf of Finland during episodic hurricanes. Storms are most frequent during the westerly wind. The climate corresponds to the marine type of temperate latitudes.

Air agitation, which usually prevails over ripple waves in the Gulf of Finland, is not strong owing to small dimension and insignificant depth of the basin. The infrequent strong agitation is generally followed by water level rise from a few centimeters to 1.0–1.2 m.

The coastal water circulation in the Gulf of Finland represents a network of several currents, including the constant current system, waves, surges, drifts, and run-offs. The constant current system, which is observed during the gulf's calm state, is a component of the general water circulation in the Baltic Sea. The current velocity ranges from 0.1 to 0.4 m/s, which is insufficient for washout and reworking of the submarine coastal slope and bottom. The semidiurnal tidal component (4 cm/s) also cannot exert a significant impact on the sediment. Hence, air agitation and surges play the dominant role in lithomorphogenesis in the eastern Gulf of Finland.

The Gulf of Finland is situated between the Baltic crystalline Shield and the Russian Plate. Pre-Quaternary rocks are characterized by a two-stage structure: the lower stage is composed of crystalline basement rocks, while the upper stage consists of sedimentary rocks of the platform cover (Amantov and Tikhomirov, 1989). Pre-Quaternary rocks are commonly overlain by Quaternary deposits represented by the Valdai moraine and glacial-lacustrine sediments (14–10 ka B.P.), clayey sediments of Lake Ancylus (10–8 ka B.P.), Litorina and Limnea seas sediments (8 ka B.P. or younger), and modern sediments (Butylin *et al.*, 1989). The Quaternary sequence reflects degradation stages of the Valdai

glacial sheet and evolution stages of the pre-Baltic basin.

Sandy sediments, which are encountered in the region as patches alternating with silty-clayey mud zones and submarine aprons of glacial and glacial-lacustrine sediments, are divided into several genetic types (Rybalko, 1985). Type 1 (relic) sand is most widespread in the northeastern Gulf of Finland. Type 2 sand, related to the present-day wave field, is observed in Zheltaya and Dubkovaya bays. Type 3 sand, accumulated in Holocene glacial depressions as a result of moraine erosion, is now encountered in the Stirsuden banks region and the southern and southeastern areas of the Berezovye Islands.

This work is based on a study of the southeastern area of the Berezovye Islands, which represent a typical example of the development of various genetic types of sand and their relationship with the present-day hydrodynamic setting and topography (Figs. 1, 2).

GRAIN-SIZE ANALYSIS

The grain-size analysis of sand was carried out in the Lithological Laboratory, VSEGEI, by the sieve method with a preliminary elutriation of the <0.01-mm fraction. Samples were divided into 21 fractions by screening through a routine set of sieves, and each fraction was weighed.

The typification of sediments is based on the following grain-size classification (mm): coarse-clastic sediment (>2.5); sand (2.0–0.05), including coarse-grained (2.0–1.0), large-grained (1.0–0.5), medium-grained (0.5–0.25), small-grained (0.25–0.1), and fine-grained (0.1–0.05) varieties; silt (0.05–0.005); and clay (<0.005) (Rybalko, 1971). Cumulative curves were plotted with Baturin's γ -scale fraction size along the X-axis and arithmetic-scale weight percents along the Y-axis. The sediment composition was approximately estimated by the median quantile method and the Trask sorting coefficient.

After normalizing the sand fraction (2.0–0.05 mm), we plotted computer-based cumulative curves and calculated the sorting coefficient (δ), mean dimension (mean arithmetic, Ma), asymmetry (Ca), and excess (E) values by the method of moments (Folk and Ward, 1957). Coefficients were based on X-values corresponding to 5, 16, 25, 50, 75, 84, and 95% values of the cumulative curve. The curves were plotted with a combination of arithmetic and Baturin (γ) scales.

$$Ma = \frac{\gamma_{16} + \gamma_{50} + \gamma_{84}}{3},$$

$$\delta = \frac{\gamma_{84} - \gamma_{16}}{4} - \frac{\gamma_{95} - \gamma_5}{6.6},$$

$$Ca = \frac{\gamma_{16} + \gamma_{84} - 2\gamma_{50}}{2(\gamma_{84} - \gamma_{16})} + \frac{\gamma_5 + \gamma_{95} - 2\gamma_{50}}{2(\gamma_{95} - \gamma_5)},$$

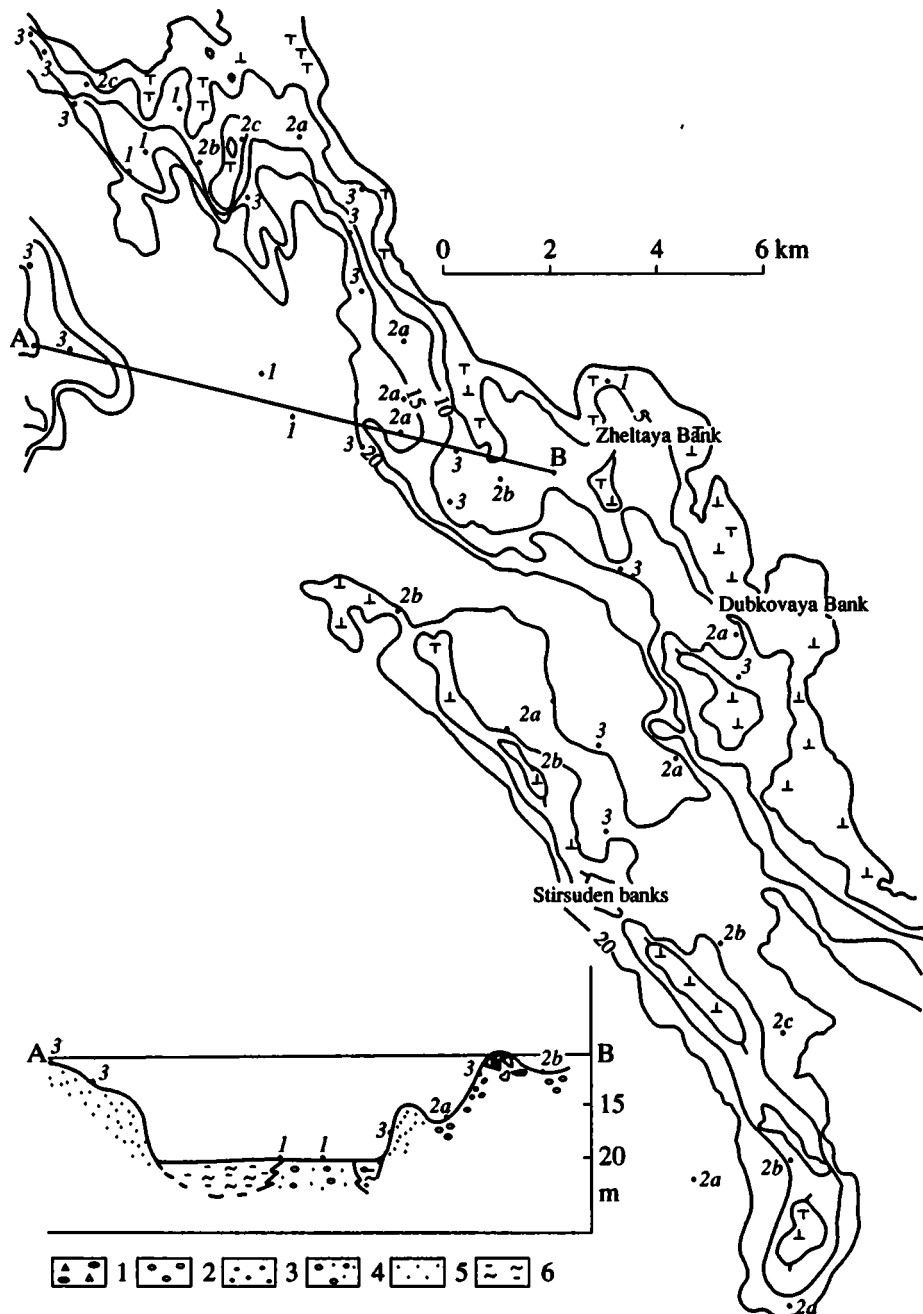


Fig. 2. Schematic distribution of sediment types, based on cumulative curves (the southern area of Berezovye Islands). (1, 2a, 2b, 2c, 3, 4) Cumulative curve types. (A-B) lithological profile. Sediment types: (1) boulders, pebbles, and gravel; (2) large- to coarse-grained sand; (3) coarse-grained sand; (4) inequigranular, mainly medium-grained sand; (5) small- to fine-grained sands; (6) silty clay.

$$E = \frac{\gamma_{95} - \gamma_5}{2.44(\gamma_{95} - \gamma_{25})} \text{ [Folk, Ward, 1957].}$$

RESULTS

The grain-size analysis of sediments based on the probability-scale cumulative curves for 229 samples

made it possible to recognize the following curve types (Fig. 3).

Type 1 (Fig. 3a) is observed in poorly sorted, large- to small-grained, medium- to small-grained, and small- to large-grained poorly sorted sands.

Type 2 is characterized by a very steep (starting) segment and a very gentle (main) segment corresponding to the fine-grained subtype 2a (Fig. 3b). Subtypes

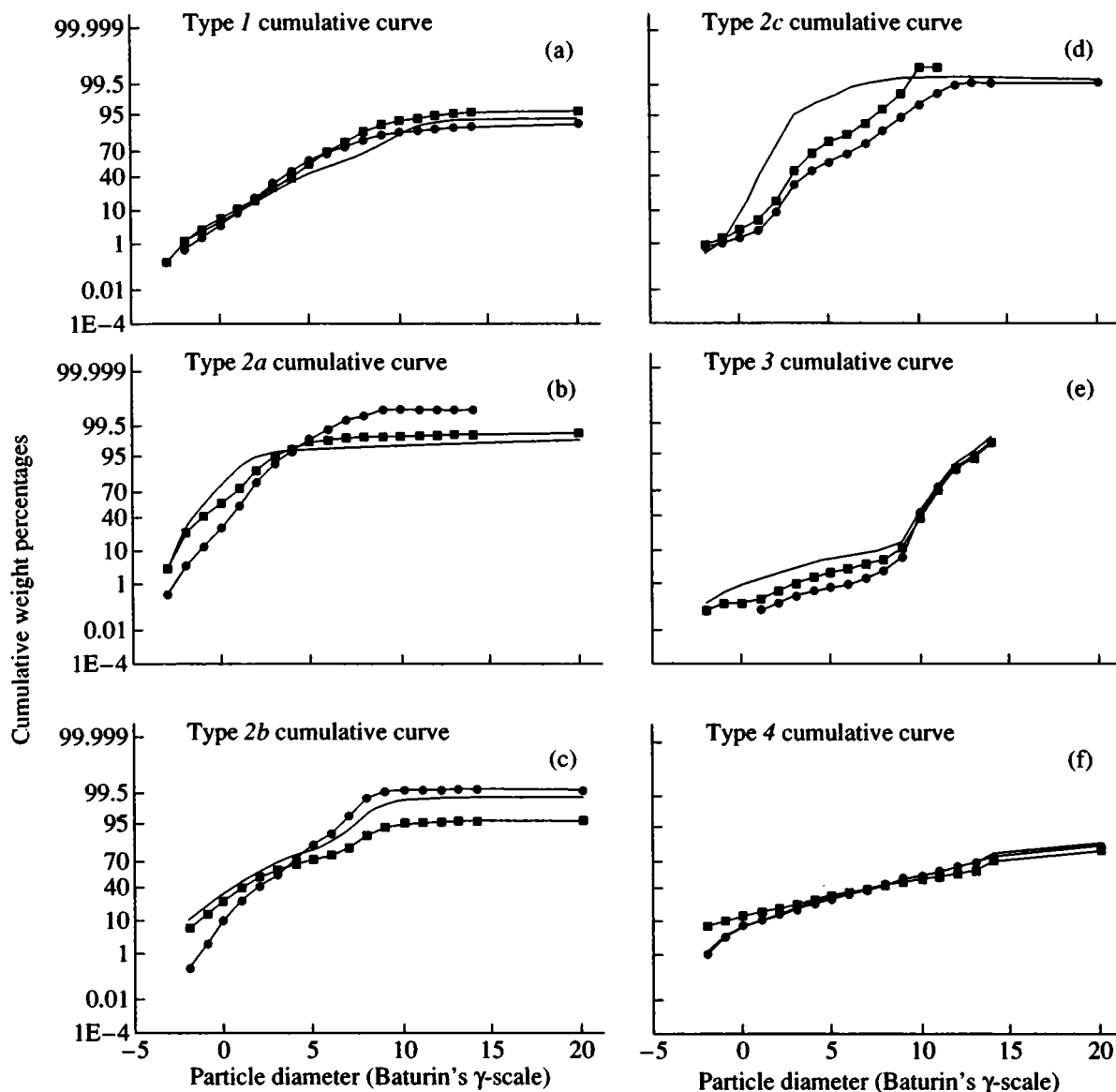


Fig. 3. Cumulative curve types: (a) 1; (b) 2a; (c) 2b; (d) 2c; (e) 3; (f) 4.

2b and 2c differ slightly from 2a by an intricate form in the medium- to small-grained region (Figs. 3c and 3d). Type 2 curves are observed in various versions of coarse- to large-grained, large- to coarse-grained, and coarse-grained sands (2a), medium- to coarse-grained and large- to large-grained sands (2b), and medium- to large-grained, coarse- to medium-grained, and large-grained sands (2c). These curves match the M_1 -type cumulative curve of the erosion zone sediment described in the literature (according to the classification of Van Aniel and Postma, 1954).

Type 3 curves (Fig. 3e), which correspond to MF-type curves in Van Aniel's classification, are typical for water edge and beach sediments, i.e., end products of the differentiation of clastic material in the coastal

(wave) zone (Rybalko, 1973). These curves are typical for the monocomponent sand of fine-grained to medium-grained dimension.

Type 4 curves represent straight lines and correspond to completely unsorted three-component sediments (Fig. 3f). According to Lider (1986), such curves are typical for *in situ* sediments.

It should be mentioned that transitional curve types (e.g., 1-2b or 2c-3) are also encountered in some cases; however, our data on a great number of samples make it possible to discriminate the above-specified cumulative curve types. Grain-size features of all curve types are given in the table.

Distribution of grain-size coefficients for cumulative curves of various types

Cumulative curve type	Median	S ₀ (Trask)	S ₀ (Folk)	Ca	E
1	4.0–9.0	1.85–2.50	3.0–3.5	–0.1...–0.5	1.0
2a	–1.6...+1.0	0.50–1.50	1.4–2.2	0.1–0.5	0.5–1
2b	–1.6...+3.0	2.05–2.60	3.0	+0.3	0.5–0.8
2c	1.5–3.5	0.7–1.25	1.0–2.0	–0.1...+0.2	0.5–0.8
3	3.0–11.0	0.55–1.5	1.1–2.4	–0.2...+0.1	0.5–1.0
4		2.9–5.65	4.5–5.0	–0.1	0.6–0.8

DATA INTERPRETATION

The analysis of the spatial distribution of sands characterized by various cumulative curve types reveals a distinct correlation with topographical features and hydrodynamic constraints (Fig. 2).

Samples characterized by cumulative curves of types 1 and 4 (except for a few samples collected near the coast or between islands) are mainly located in submarine ravines and open sectors of the gulf (isobaths deeper than 20 m) that are not affected by air agitation and currents. These distal zones are only occasionally disturbed by strong storms. Present-day hydrodynamic conditions are unfavorable for sand accumulation in such zones. Sediments described above are represented by up to 1-m-thick relic sand deposits in the immediate vicinity of modern silty-clayey accumulations. According to Emery (1968), relic sand represents the present-day shelf sediment formed by wave, abrasion, alluvial, or glacial processes at the final stage of the Pleistocene Glaciation in zones shallower than the present-day ones, i.e., in environments differing from modern ones. In the eastern Gulf of Finland, relic sand was probably formed approximately 10 ka B.P., during the lowest water level, as a result of the breakthrough of the Baltic glacial lake water (Rybalko, 1985). Since the relic sand was formed as a result of the washout of sandy facies of glacial-lacustrine sediments in a more active hydrodynamic regime (relative to the modern one), it is characterized by a small thickness and poor sorting.

Type 4 curves correspond to completely unsorted sandy sediments that are deposited in zones beyond the influence of air agitation and currents. The almost rectilinear shape of the cumulative curve and the abundance of fine-grained material (15–20%) suggest an absence of present-day erosion processes.

In contrast to sediments described above, relic sand with a type 1 cumulative curve was partly subjected to the submarine washout. This is suggested by both the cumulative curve shape, which is typical for an environment characterized by the loss of fine-grained sand fractions, and the lesser content of silt-clayey material (the <0.01-mm particles do not exceed 5%).

Sand with the type 2 cumulative curve is characterized by good, medium (2a, 2c), or poor sorting. Depending upon the initial material composition, it is represented by the two- or three-component varieties and ranges from the coarse- and large-grained (2a) sands to large- and medium-grained (2c) sands. Type 2 sand is accumulated on submarine rises or near coastal zones. In both cases, it is adjacent to the hypsometrically higher coarse-clastic sediment, which covers submarine rises and the coastal slopes of capes. Thus, type 2 sediment is located in a palimpsest facies environment. Since the formation of this sediment is governed by waves and currents of diverse types and directions, its reworking grade is highly heterogeneous. Differences between 2a, 2b, and 2c subtypes described above are apparently induced by the influence of diverse processes at different stages of sedimentation. Sand with type the 2 cumulative curve is most widespread in the Stirsuden banks region, where the fluvio-glacial sand is currently located in washout zones.

The type 3 curve is observed in sediments from very steep submarine slopes of both coastal and submarine rises. These sectors are characterized by an intense hydrodynamic activity (particularly, air agitation and associated submarine currents); i.e., they represent modern wave-related zones with well-sorted multicomponent sediments ranging from medium- to fine-grained varieties, depending upon the nature of the initial material.

Thus, the data described above make it possible to propose the following scheme of facies environments:

(1) Peaks of submarine banks and coastal sectors (up to an isobath of 5 m) covered by rubble and pebbles. The erosion of slopes in these zones is hampered by the coarse-clastic cover representing a highly stable material.

(2) Transitional zones (depth 5–20 m) located below the coarse-clastic zone and composed of sand with a low- to medium-grade sorting. Owing to the action of diversely oriented air agitation and currents and the abundance of coarse-clastic material, the palimpsest-facies sediments here are characterized by heterogeneous sorting (type 2 cumulative curve).

(3) Submarine slopes (10–20 m) characterized by an intense wave- and current-related sedimentation. They

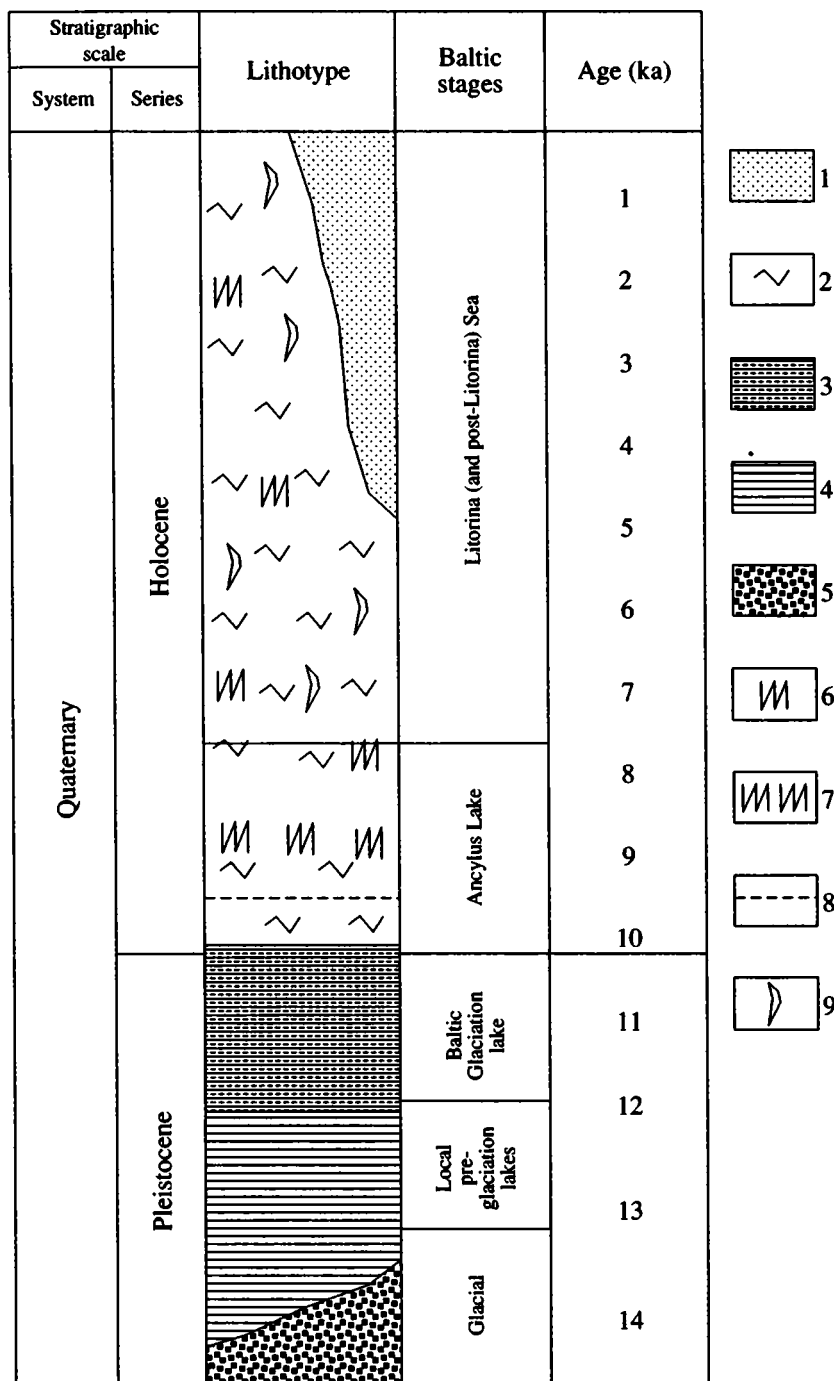


Fig. 4. Stratigraphic column of Upper Quaternary sediments in the northeastern Gulf of Finland. (1) Sand; (2) clay; (3) layered clay; (4) ribbon clay; (5) moraine; (6) organic matter accumulation; (7) organic matter interlayer; (8) hydrotroilite; (9) shell detritus.

are composed of well-sorted sand and represent zones of modern wave-related accumulation (type 3 cumulative curve).

(4) Submarine ravines and open sectors of the gulf with a significant depth (more than 20 m). Here, the hydrodynamic influence of waves on sediments is negligible, and zones with an unstable hydrodynamic equilibrium of palimpsest facies are locally encountered. In

this case, accumulative processes are suppressed as a result of the absence of clastic material sources and limited areas of submarine erosion. Since the submarine erosion is subordinate, the fine-grained fraction of relic sand is eroded only (type 1 cumulative curve).

(5) Zones beyond the influence of agitation and currents. Although they are located near present-day sedimentation sectors, they represent transit zones where

the sedimentary material is not accumulated. The presence of such zones is related to the fact that the stable nepheloid sedimentation in the Gulf of Finland is generally active below the 30-m isobath. Such transition zones can be characterized by a short-term silting during the summer; however, the silty-clayey material is further transported during strong autumn and winter storms and is redeposited in deeper basins of the open sea. Such zones incorporate submarine outcrops of Upper Pleistocene glacial-lacustrine clays and relic unsorted (three-component) sands that were not apparently subjected to an active hydrodynamic reworking (type 4 cumulative curve). These sediments correspond to the distal facies (depth more than 20–30 m) and are not shown in Fig. 2.

(6) Deeper zones of the present-day nepheloid accumulation of silty and clayey muds (20–60 m).

CONCLUSION

The lithological mapping based on the cumulative curve method made it possible to compile lithofacial maps of the Gulf of Finland. Cumulative curves obtained are divided into four major types and several subtypes. Each curve type corresponds to a sand variety with specific dimension, sorting grade, and statistical parameters. The cumulative curves and their genetic interpretation are in good agreement with the literature data.

Sediments with different types of cumulative curve occupy specific positions in the bathymetric profile. Therefore, cumulative curves can be correlated with specific hydrodynamic constraints. In other words, sands accumulated in submarine ravines under the influence of water currents, on submarine slopes characterized by active erosion and redeposition processes, or in zones under the influence of agitation are characterized by specific cumulative curve patterns. The mapping of sediments with different types of cumulative curve makes it possible to reconstruct their facies environments.

The proposed method offers a tool for the more comprehensive utilization of genetic criteria during the lithological mapping of modern sands. Additionally, it can be used in paleogeographic reconstructions during paleodynamic analysis. The application of computer-based methods allows a rapid processing of large arrays of grain-size data.

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Manganese Carbonates in Recent Sediments: Geochemistry of Isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) and the Origin

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Abstract—The isotopic composition of manganese carbonates is studied in recent sediments from various basin types: oceanic (Guatemala Basin and Middle America Trench, Pacific Ocean); marine (Baltic Sea and White Sea); and lacustrine (Punnus Jarvi, Karjala Isthmus). The isotope data indicate that authigenic manganese carbonates are formed within the diagenetic zone, and that organic carbon actively participates in this process. The carbon isotopic composition in these carbonates is controlled by a local relationship between sedimentary carbonate material and oxidized organic carbon. The oxygen isotopic composition is determined by the oxygen composition in the interstitial water that completely exchanges with bottom waters in the upper mud layer (early diagenetic zone). The isotope data available allow us to conclude that the carbonate manganese ore formation, resulting in large manganese ore deposits (such as Nikopol, Mangyshlak, and others), might only take place under conditions close to those existing in intracontinental and marginal seas.

From both scientific and practical points of view, it is important to elucidate formation conditions and distribution patterns of manganese carbonates in recent sediments, so far as the largest industrially mined manganese deposits of sedimentary (or sedimentary–hydrothermal) genesis are mainly represented by carbonate ores and their oxidation products.

Different, and sometimes diametrically opposite, concepts exist upon the origin of manganese deposits and formation conditions of manganese ores themselves. In order to apply the actualistic principle, we have to ascertain, first of all, the general geological and geochemical formation conditions of Mn-bearing carbonates in different types of recent sediments. Data on oxygen and carbon isotopes provide important information for the solution of this problem.

Recent ferromanganese ore formation is known to be rather widespread, and a large number of publications dealing with this problem by both Russian and foreign scientists is available. The ore-forming processes take place both on the World Ocean floor and in marginal and intracontinental basins (seas, lakes). These ore accumulations are mainly represented by various crustal and nodular forms of ferromanganese oxides, whereas carbonates are more rare. The ores are largely of diagenetic origin, and are characterized by certain mineralogical–geochemical features reflecting specific conditions of their formation (basin type, location, source of ore material, etc.).

Manganese accumulation in the form of authigenic carbonates with a complicated composition is also a rather widespread phenomenon in Pleistocene–Holocene sediments of lakes, seas, and near-continental oceanic areas. These carbonates are characterized by variable contents of Mn, Ca, Mg, and Fe. In particular,

it is assumed that favorable conditions for authigenic manganese carbonate (rhodochrosite) formations are created during the diagenesis of sediments with low organic matter (OM) content (Logvinenko *et al.*, 1972). Such conditions are observed in the ocean within the transition zone from strongly reduced near-shore sediments to oxidized pelagic ones.

MANGANESE CARBONATES IN OCEANIC SEDIMENTS

At present, isotope geochemistry is best studied in manganese carbonates from Pacific sediments. Manganese-bearing carbonates were recovered in cores of several boreholes drilled by the *Glomar Challenger* off the Peru coast (Guatemala Basin) in the Pacific Ocean. Isotope studies carried out on Mn-bearing carbonates from this region by Coleman *et al.* (1982), as well as some isotope data by other authors (Pedersen and Price, 1982), showed a substantial difference in carbon isotope from that of proper sedimentary carbonates, which are in equilibrium with seawater bicarbonate.

The author, together with V.N. Sval'nov, studied in detail Ca-rhodochrosites from this region. Isotopy of manganese carbonates from other regions of the Pacific is rarely studied, and only minimal, separate data are available (Pedersen and Price, 1982).

Isotopic Composition and Origin of Calcium Rhodochrosite in Sediments from the Guatemala Basin

Presently, sediments off the Peru coast, Pacific Ocean, including ferromanganese nodules from the Guatemala Basin, are rather well studied. Many publications on the subject, mainly by Russian scientists,

appeared during last years (Dubinin and Sval'nov, 1995; Morozov, 1995a, 1995b; Skornyakova and Uspenskaya, 1989; Skornyakova *et al.*, 1996; Sval'nov, 1994, 1995; Sval'nov and Novikova, 1995; Uspenskaya *et al.*, 1995; and others).

We also studied sediments from the Guatemala Basin, within a survey area centered at 6°30'N, 92°00'E (Sval'nov and Kuleshov, 1994). Specific features of the studied area are the following: (1) upper 10–25 cm of the sediment are highly enriched in Mn; (2) ferromanganese nodules occur both at the sediment surface and within the sedimentary sequence; (3) products of acidic volcanism are widespread; (4) variegated sediments are replaced by gray ones along the northern margin of the survey area; and (5) silica content is rather high, and carbonate content is variable in the sediments. The homogeneous surface layer of the sequence, calcareous at some sites, is represented by a dark brown clayey radiolarian ooze, often rich in diatoms. Radiolarian diatomaceous ooze occurs locally. The thickness of the homogeneous surface layer varies from 2–11 cm. A variegated and bioturbated sequence, with a variable oxidation degree, is located below. Brown, light brown, and pale yellow shades of color predominate in the variegated sequence. At several stations, yellowish gray or greenish gray sediments are located below 30–70 cm.

Quaternary sections are dominated by a clayey radiolarian ooze, often slightly calcareous and locally rich in diatoms. Interbeds of foraminiferal–nannofossil ooze (rich in radiolarians) and radiolarian–diatomaceous ooze also occur.

The macroscopic and microscopic study of collected samples from several stations (3850, 3884, 3899), revealed segregations and small aggregates of authigenic manganese carbonate crystals. Such characteristics are observed in different types of sediments displaying the residual C_{org} content 0.3–1.6%, low carbonate content ($CaCO_3$ less than 1.83%), and Mn content 0.4–4.5%.

Composition of authigenic manganese carbonate. A detailed study of sediments (using the immersion method and scanning electron microscopy) showed that authigenic carbonate is represented by spheroidal aggregates. Intergrowths of spheroidal manganese carbonate aggregates are clearly observed. Based on X-ray diffraction data (Fig. 1), one can suggest that the specimens studied consist of rhodochrosite (Fron del and Bauer, 1955; Silaev *et al.*, 1993; Vasil'ev and Vasil'eva, 1980). Increased basal reflection (2.899–2.1912 Å) is evidence of the partial isomorphic replacement of Mn ions in rhodochrosite with Ca and Mg ions. The purest rhodochrosite is found at Station 3850. The presence of rhodochrosite is also confirmed by analyzing the chemical composition of authigenic aggregates (Sval'nov and Kuleshov, 1994). For example, based on the sum adjustment of carbonate components to 100%, the approximate mineral formulas in specimens from dif-

ferent concentric zones (of a zonal nodule) found at Station 3899 are as follows:

(1) $(Mn_{60.7}Ca_{32.5}Mg_{6.5}Fe_{0.3})CO_3$ in friable nodule; (2) $(Mn_{60.4}Ca_{32.7}Mg_{6.6}Fe_{0.3})CO_3$ in friable outer cover of the nodule; and (3) $(Mn_{64.6}Ca_{32.4}Mg_{2.8}Fe_{0.2})CO_3$ in dense internal part of the nodule.

Thus, the authigenic carbonate in sediments from the Guatemala Basin is represented by Ca-rhodochrosite, with a considerable admixture of Mg. Rhodochrosite found earlier in the same basin (Lynn and Bonatti, 1965) is of a similar composition: $(Mn_{50-80}Ca_{20-50})CO_3$. At DSDP Site 503 (southern Guatemala Basin), numerous Ca-rhodochrosite nodules occur in Upper Miocene to Holocene reduced sediments (Coleman *et al.*, 1982). These authors suggest that rhodochrosite is formed near the bottom surface, due to interaction of bicarbonate of bottom water and highly concentrated interstitial water with Mn^{2+} .

Isotope data. The Guatemala Basin is known for an abundance of manganese carbonate in recent sediments. The isotope data available (Coleman *et al.*, 1982; Pedersen and Price, 1982) are related to carbonates only from this region.

Coleman *et al.* (1982) studied, in detail, the chemical composition and carbon and oxygen isotopes in 17 samples of Mn-rich carbonates recovered in holes 503A and 503B (southern Guatemala Basin). The isotopic composition in these samples varies from –3.8 to –1.2‰ for $\delta^{13}C$, and from 34.87 to 36.50‰ for $\delta^{18}O_{SMOW}$ (or from 4.06 to 5.99‰, relative to PDB standard). Our isotope data (Sval'nov and Kuleshov, 1994) are similar: $\delta^{13}C$ values vary from 2.5 to –1.1‰, and $\delta^{18}O$ values range within 34.9–37.1‰, relative to the SMOW standard (Fig. 2).

The above isotope data differ considerably, by higher $\delta^{13}C$ values, from those characteristic for lacustrine and marine manganese carbonates. It is impossible today to compare the isotopic composition of studied rhodochrosites with that of analogous carbonates from other parts of the World Ocean. However, the isotopy of rhodochrosites from the Guatemala Basin sediments differs substantially, by their higher values of the heavy isotope ^{13}C , from that of analogous carbonates from other basin types. This is likely related to specific formation conditions of manganese carbonate in sediments from the Guatemala Basin.

It is ascertained that practically all known sedimentary manganese carbonates (both fossil and recent varieties of marine and lacustrine formations) are characterized by low $\delta^{13}C$ values (Kuleshov and Chistyakova, 1989; Kuleshov and Dombrovskaya, 1988, 1990, 1993, 1997; Kuleshov and Shterenberg, 1988; Kuleshov *et al.*, 1991). The reason is that manganese carbonates are formed in sedimentary sequences at the diagenetic stage, when isotopically light carbon dioxide participating in the process is generated within the sediment itself as a result of OM oxidation. Because of this, we can suggest that manganese carbonates were formed in

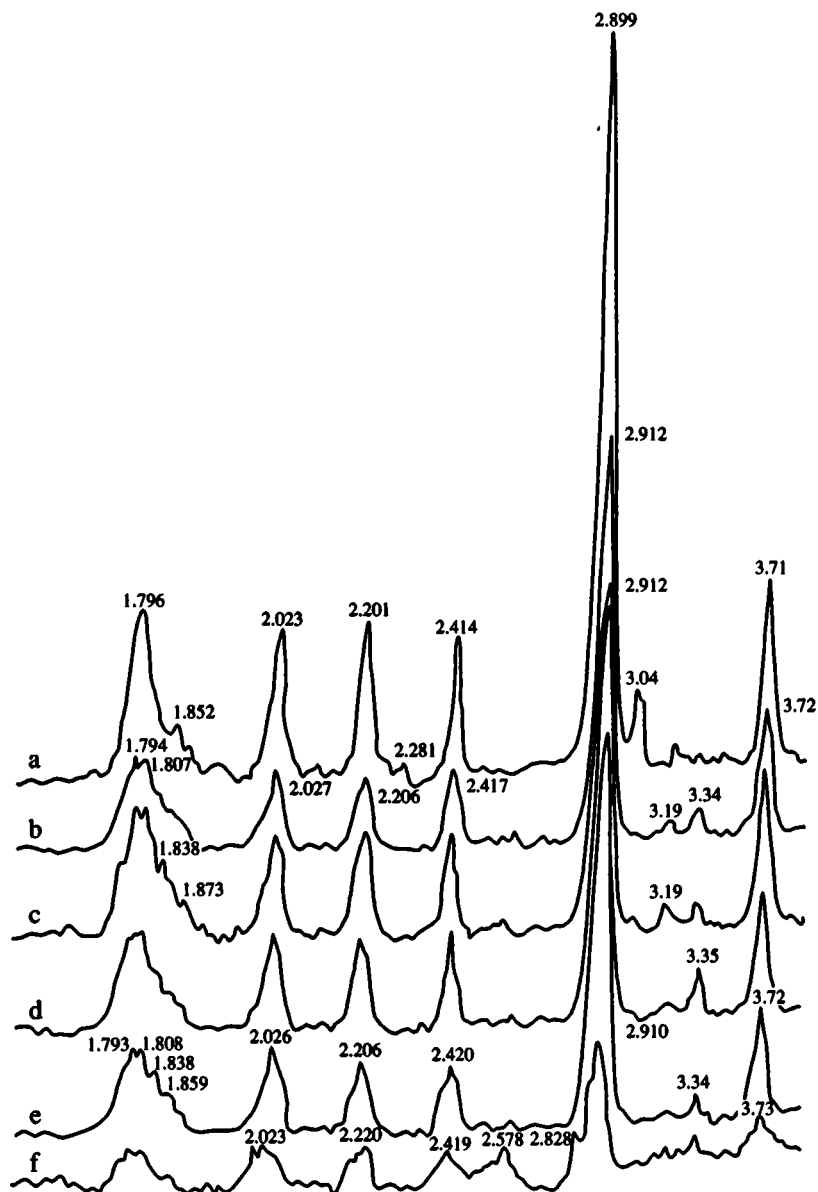


Fig. 1. X-ray diffraction patterns of carbonate nodules from the Guatemala Basin sediments, Pacific Ocean (Sval'nov and Kuleshov, 1994). (a) Yellowish white nodule, Station 3850, interval 330–340 cm; (b) yellowish gray flat nodules, Station 3884, interval 249–255 cm; Station 3899, interval 295–300 cm; (c) brownish gray friable nodule, (d) brownish gray friable crust of the nodule, (e) gray dense internal part of the nodule, (f) contact of rhodochrosite and ferromanganese nodule.

Guatemala Basin sediments in other, rather specific conditions of diagenesis, in which the role of organic CO_2 was negligible. Manganese carbonates were mainly formed as a result of dissolution and redeposition of biogenic calcium carbonate (likely foraminiferal tests and calcareous skeletal remains of other organisms) in sediments.

In some samples, we studied different genetic varieties of manganese carbonate within a single sample. The $\delta^{13}\text{C}$ values of rhodochrosite in a carbonate nodule and host sediment from Station 3899, core interval 295–340 cm, range from -2.5 to -2.0‰ . In some nod-

ules, the internal part is characterized by higher $\delta^{13}\text{C}$ values (-1.9‰), as compared with the outer part (-2.3‰). Similar results were earlier obtained by Coleman *et al.* (1982): an increasing trend of $\delta^{13}\text{C}$ values, from the periphery to the center, was registered for two nodule samples among the five studied.

The $\delta^{13}\text{C}$ value increases downward the section in nodules from the core at Station 3899: -2.5‰ at 295 cm; -1.9‰ at 301–306 cm; and -1.1‰ at 330–340 cm. Overall, the isotopic composition of manganese carbonates does not depend on their occurrence forms in sediments (nodules, disperse material, or others). Neg-

ligible variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values observed both in different samples, and within a single nodule, are likely related to local changes in conditions of manganese carbonate formation (permeability of sediments, physicochemical heterogeneity, etc.) as it was previously suggested by Coleman *et al.* (1982).

For comparison, we also studied carbon and oxygen isotopes in foraminiferal tests separated from both host sediments and manganese carbonate nodules themselves. A stable difference was revealed between the isotopic composition of foraminifers and that of manganese carbonates from nodules. Foraminifers are commonly characterized by higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (by about 2–3‰), as compared with those detected in nodules. Such a difference likely results from the different isotopic composition of initial bicarbonate, and from the temperature of carbonate precipitation.

It is well known that bicarbonate is commonly characterized by heavier $\delta^{13}\text{C}$ values, in upper layers of the water column, as a consequence of their higher biological productivity. Because of this, the carbonate of foraminiferal tests, which use bicarbonate from upper layers of the water column during growth, must show heavier $\delta^{13}\text{C}$ values. This explains the position of foraminiferal data points in Fig. 2. In some cases, the carbonate of foraminiferal tests enclosed in nodules may undergo recrystallization during diagenesis. Consequently, isotopic composition can become lighter, as it is well demonstrated in the plot.

Thus, the isotopic data available allow us to conclude that the carbon dioxide of studied rhodochrosites was largely adopted from a sedimentary calcium carbonate of foraminiferal tests and from skeletal remains of other organisms as a result of their dissolution and reprecipitation. Isotopically light, organic carbon dioxide (formed as a result of C_{org} oxidation) plays a subordinate role in the formation of authigenic carbonates. Host sediments served as a source of Mn for carbonate nodules. Ferromanganese nodules also delivered Mn during diagenetic remobilization.

Manganese carbonates formed in Guatemala Basin sediments under specific conditions characterized by the low geochemical activity of organic matter that resulted in relatively high $\delta^{13}\text{C}$ values in the studied nodules.

Manganese Carbonates in Sediments from the Middle America Trench (El Gordo Rise)

Shterenberg *et al.* (1992) studied sediments from the oceanic slope of the Middle America Trench collected at Station 82105 (18°08.3'N, 104°43.2'W, water depth 4300 m). The core was 457 cm long. Sediments were represented by aleuritic mud with an admixture of volcanoclastic material. Iron sulfides were rather abundant in the 300–457 cm interval of this core, as well as in lower parts of cores from neighboring stations (82108, 82101, and 8296).

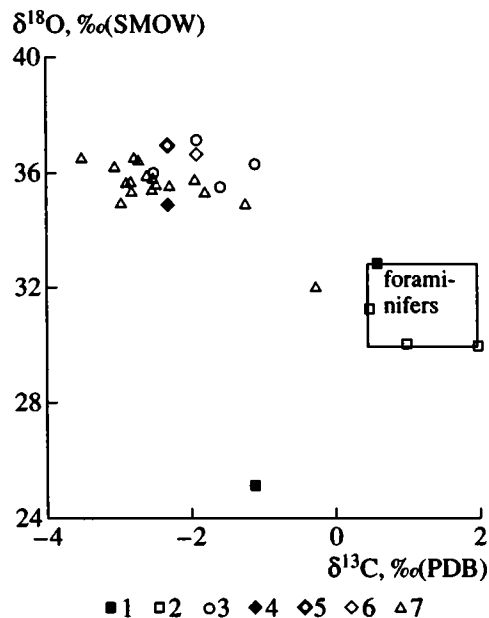


Fig. 2. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate nodules from the Guatemala Basin (Pacific Ocean). (1) Foraminifers from nodules; (2) foraminifers from host sediments; (3) nodules from stations 3884, 3895, and 3899; nodule from Station 3899, interval 295–300 cm; (4) friable nodule, (5) crust of the nodule, (6) central part of the nodule; (7) data by Coleman *et al.* (1982).

The MnO content in sediments of the studied core was highest within the 15–25 cm interval, where manganese oxides and carbonates were observed in size fraction >0.1 mm. The Fe^{2+} content increased downward the section. This observation is in agreement with data on the obvious domination of iron sulfides (mainly pyrite) in a fraction >0.1 mm from the lowermost interval (400–430 cm). The iron sulfide content in fraction >0.1 mm was lower within the 240–250 cm interval, and it was even less in the upper part of the section. The Ca content was somewhat higher in the 15–25 cm interval, as compared with other intervals. However, an extremely low CO_2 content (0.65%) does not allow the relation of high Ca content to carbonates. Amounts of other elements are similar in different intervals.

Various morphological types were identified among the manganese carbonates in a fraction >0.1 mm: (1) relatively thin (<1 mm) crust-like grains and their fragments; (2) commonly light-colored, small (<0.1 mm), dense grains, which represent sediments cemented by manganese carbonate and are partially oxidized at the outer surface; (3) light-colored (pinkish white, yellowish white) manganese carbonate inclusions within a gray sediment; and (4) small elongated (<1 mm long) carbonate aggregates similar in appearance to bunches of grapes.

The mineral composition of the bunch-like variety of carbonates was studied using X-ray diffractometry. Diffraction patterns for several specimens are shown in

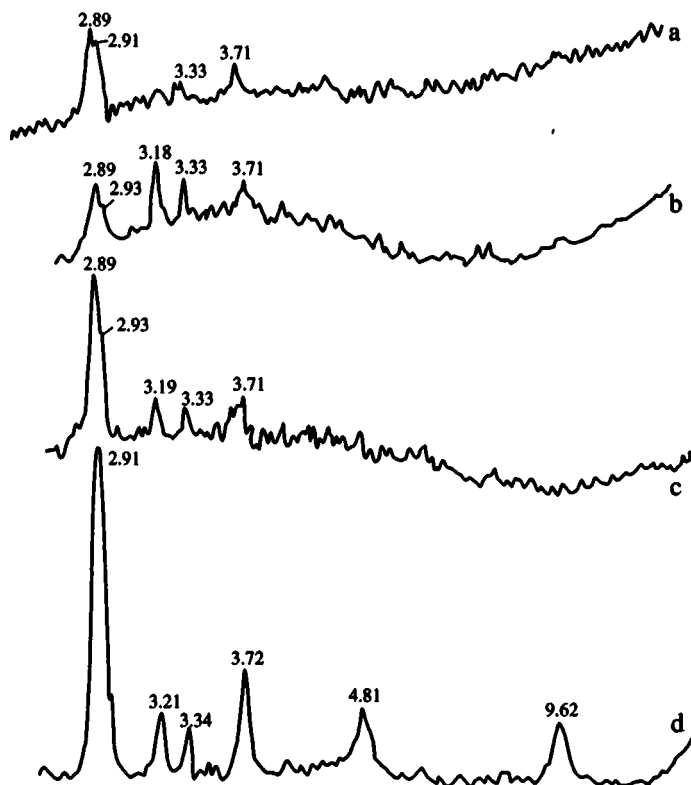


Fig. 3. X-ray diffraction patterns of manganese carbonates from the El Gordo Rise, Middle America Trench, Pacific Ocean (Shterenberg *et al.*, 1992). (a, b) Manganese carbonate crusts; (c) small separated carbonate nodules in muddy sediment; (d) manganese oxide-carbonate segregations.

Fig. 3. They indicate a polymineral composition of the carbonate material dominated by Ca-rhodochrosite characterized by the main reflection varying from 2.89 to 2.93 Å. Reflection 2.96–2.97 Å indicates that manganoalcite is also possibly present in the sample.

Results of chemical analyses and their recalculation allowed us to distinguish three main groups of manganese carbonates with different contents of major and minor cations (Shterenberg *et al.*, 1992): (1) $(\text{Mn}_{53}\text{Ca}_{41}\text{Mg}_6)\text{CO}_3$; (2) $(\text{Mn}_{58}\text{Ca}_{39}\text{Mg}_3)\text{CO}_3$; and (3) $(\text{Mn}_{61}\text{Ca}_{37}\text{Mg}_2)\text{CO}_3$.

Thus, manganese carbonates found in the upper layer of sediments from the oceanic slope of the Middle America Trench (Station 82105), are rather similar to diagenetic counterparts from the hemipelagic zone of other Pacific regions in chemical and mineral composition. The role of diagenetic processes in the manganese carbonate formation is also confirmed by studies of the interstitial water extracted from several intervals of the sediment core (Shterenberg *et al.*, 1992).

The sample for isotope study was selected from the interval with highest Mn content (15–25 cm). The isotope relations obtained are the following: $\delta^{13}\text{C}_{\text{PDB}} = -6.01\text{‰}$; $\delta^{18}\text{O}_{\text{SMOW}} = 35.06\text{‰}$. As follows from mineralogical-geochemical observations, these values belong to rhodochrosite.

The isotope data obtained are characterized by a lighter carbon isotopic composition, as compared with that in rhodochrosites from the Guatemala Basin. This is evidence of a considerable contribution of C_{org} into the carbon composition of carbonates, and consequently, indicates a more active role of organic matter in the diagenesis.

MANGANESE CARBONATES IN MARINE SEDIMENTS

Manganese Carbonates in Baltic Sea Sediments

Since the finding of Mn-bearing carbonates in deep-water sediments of the Baltic Sea (Gorshkova, 1967), their mineralogy, geochemistry, and other genetic aspects have been studied in detail. However, isotopes in manganese carbonates are not yet sufficiently studied. Suess (1979) studied carbon isotopic composition in a rhodochrosite sample from the Landsort Deep. The $\delta^{13}\text{C}$ value obtained was rather low (-13‰). Based on this and data on other carbonates from the Baltic Sea sediments, he suggested a diagenetic origin of the manganese carbonate, with an active participation of organic carbon dioxide (i.e., CO_2 generated during microbial decomposition of OM) in the process.

We studied carbon and oxygen isotopic composition in the carbonate constituent of sediments recovered by

the gravity core at Station 3173, from the central part of the Gotland Deep (57°20.9'N, 20°18.8'E), at a water depth of 243 m (Kuleshov and Rozanov, 1998).

Holocene sediments at the station are represented by greenish gray and dark gray pelitic mud, which are underlain by late glacial bluish gray clay at a depth of 168 cm below sea bottom. The sediments are strongly reduced ($E_h = -200$ mV). They are enriched in organic matter ($C_{org} = 9.9\text{--}5.79\%$), and contain free hydrogen sulfide that penetrates into and strongly reduces the underlying sequence of late glacial clay ($E_h = -280$ mV). It should be noted that the diffusive penetration of hydrogen sulfide takes place against the background of lower organic matter content, characteristic for this period of sedimentation (C_{org} content is commonly about 0.5%).

Authigenic carbonates in sediments from deep basins of the Baltic Sea have complicated compositions. X-ray diffraction measurements in powder specimens revealed a presence of carbonates, corresponding to the isomorphous mineral series ranging from calcite and dolomite to rhodochrosite and ankerite. According to calculations by Manheim (1961), the composition of studied carbonate from dark green mud (Station S-33, depth 188 m) corresponds to the formula $(Mn_{72}Ca_{16}Mg_{12})CO_3$.

Suess (1979) obtained a similar composition of authigenic carbonate in deep-water sediments from the Landsort Deep: $Mn_{85}Ca_{10}Mg_5$. According to Calvert and Price (1977), the composition of mixed carbonate in Baltic sediments varies from $Me_{60}Mn_{40}CO_3$ to $Me_{10}Mn_{90}CO_3$, where Me depicts bivalent cations of Ca, Mg, and Fe. Hartmann (1964) presented a somewhat different formula for the mixed carbonate, including Fe into the composition: $(Mn_{56.8}Ca_{25.46}Mg_{9.72}Fe_{8.02})CO_3$.

The composition of authigenic carbonates from Station 3173 also represents an isomorphous mixture. According to data by E.M. Emel'yanov *et al.* (1986), mixed carbonates, close to compositions $Me_{0.3}Mn_{0.7}CO_3$ and $Me_{0.2}Mn_{0.8}CO_3$ (where Me depicts cations Ca^{2+} , Mg^{2+} , and Fe^{2+}), occur in this core, except for samples with low Mn and C_{org} content. Previous X-ray diffraction measurements showed that below the subbottom depth of 1 m, the carbonate of a mixed composition is replaced by poorly crystallized rhodochrosite (Emel'yanov and Pustel'nikov, 1975).

We carried out X-ray diffraction measurements (analyst E.V. Pokrovskaya, GIN) in air-dry powder specimens of sediments with the highest Mn and CO_2 content from core intervals 40–51 cm (Sample 2122) and 150–155 cm (Sample 2126). It appeared that reflections characteristic for carbonate minerals are absent in the X-ray diffraction pattern of Sample 2122. Meanwhile, the reflection corresponding to lattice spacing 2.886 Å, and less intensive ones corresponding to spacings 3.69, 2.409, 2.194, 2.021, and 1.790 Å are well detectable in Sample 2126.

Considering the high Mn content in the sediment, we can suggest that such a series of reflections best corresponds to rhodochrosite or kutnahorite, a manganese mineral with a dolomite structure (Prondel and Bauer, 1955; Silaev *et al.*, 1993). However, we believe that the crystalline carbonate in the sediments studied is represented by rhodochrosite with a minor isomorphous admixture carbonate of Ca, Mg, and Fe. A more correct solution of the problem requires additional and special investigations, which are beyond the scope of this work.

Thus, both results of previous studies and our recent data indicate that authigenic carbonates in sediments from the Baltic Sea depressions are represented by an isomorphous mixture of minerals, ranging from calcite and dolomite to rhodochrosite and siderite. The carbonates are X-ray amorphous in upper sediment layers, and their crystallization (likely incomplete) is only observed in the lower part of Holocene deposits.

Isotope data. The carbonates studied from the Gotland Deep are characterized by minor variations in $\delta^{13}C$ (–9.1 to –6.9‰) and $\delta^{18}O$ (28.8 to 30.1‰). The samples are substantially enriched in the light carbon isotope ^{12}C , as compared with normal marine sedimentary carbonates. Such isotope patterns are generally characteristic for carbonates of diagenetic origin. The enrichment of carbonates in light carbon isotope is caused by a contribution of isotopically light biogenic carbon dioxide (generated as a result of OM oxidation during diagenesis) in their formation.

As noted above, similar data on carbon isotopic composition were obtained earlier by Suess (1979) for rhodochrosite from the Landsort Deep. The $\delta^{13}C$ value determined by this author is somewhat lower (–13‰), as compared with our data. According to conclusions by Suess, as well as by Force and Cannon (1988), the light isotopic composition of these carbonates and their forms of occurrence in sediments are both evidence of the carbonate formation due to replacement of carbonates in interstitial water, with a presence of decomposed OM.

Lein *et al.* (1986) studied the isotopic composition of organic and mineral carbon in Baltic Sea sediments. According to their data, $\delta^{13}C$ values of the total carbon dioxide vary from –21.6 to –8.1‰; and in sediments from the Gotland Deep, they range from –18.1 to –8.1‰. These authors conclude that anaerobic microbial OM decay is the source of isotopically light carbon dioxide in sediments. They attribute observed variations in $\delta^{13}C$ values to various contributions of genetically different types of carbon (derived from microbial CO_2 , sedimentary carbonates, or organic matter of sediments) in diagenetic carbonate formation.

Oxygen isotopic composition in the carbonates studied is rather uniform along the section. A minor increase in light oxygen isotope ($\delta^{18}O$ up to 28.8‰) is only noted at a subbottom depth of 100–120 cm.

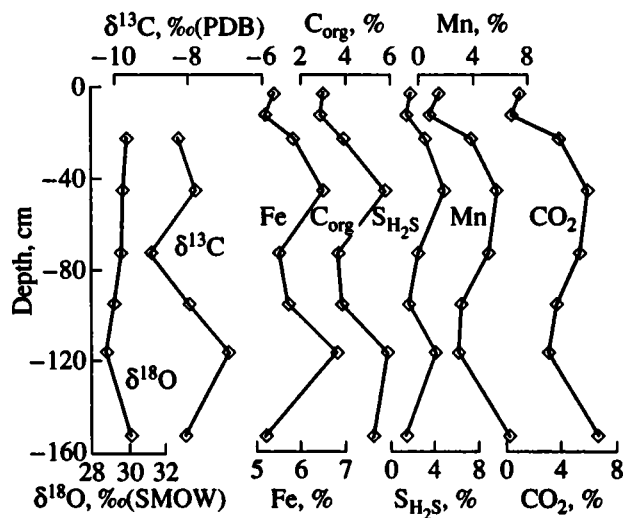


Fig. 4. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in manganese carbonates and chemical composition of sediments from Hole 3173, Baltic Sea (Kuleshov and Rozanov, 1998).

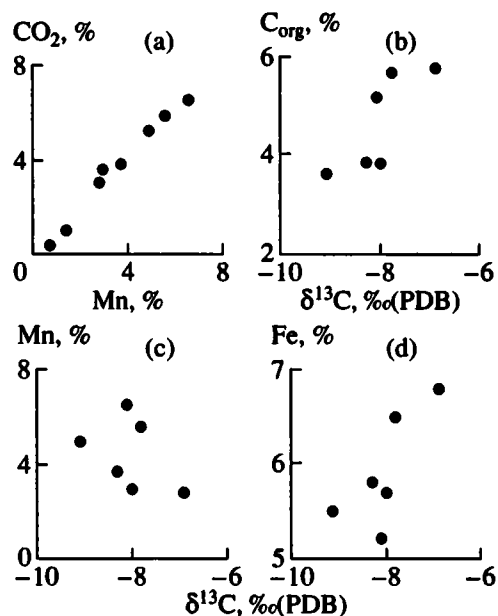


Fig. 5. Relationships in sediments from Hole 3173, Baltic Sea: (a) CO_2 vs. Mn; (b) $\delta^{13}\text{C}$ vs. C_{org} ; (c) $\delta^{13}\text{C}$ vs. Mn; and (d) $\delta^{13}\text{C}$ vs. Fe.

Unlike oxygen isotopy, carbon isotopic composition is unevenly distributed in the core section. Observed deviations (peaks) of $\delta^{13}\text{C}$ values generally correlate with the chemical composition of sediments (Fig. 4). One can see a direct correlation of $\delta^{13}\text{C}$ values with the contents of Fe_{bulk} , C_{org} , and less distinctly, with S_{pyr} ; and a reverse correlation with the contents of Mn and CO_2 (Fig. 5). As repeatedly noted before (Emel'yanov *et al.*, 1982, 1986), the Mn concentration distinctly correlates with CO_2 content. The correlation between carbon iso-

topy and the chemical composition of sediments noted above, is possible evidence of a complicated and interdependent geochemical redistribution of chemical components (within the diagenesis zone) that can be considered as a closed geochemical system, relative to the elements under discussion.

The authigenic origin of carbonate constituents in Holocene sediments from deep depressions of the Baltic Sea is undoubted. This is supported both by available published isotope data (Botther and Huckride, 1991; Lein *et al.*, 1986; Sohlenius *et al.*, 1996; Suess, 1979) and by our data on oxygen and carbon isotopy. However, the regularities in variations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonates along the Holocene section, obtained during our study, as well as the ascertained correlations between isotopy and chemical composition of sediments, allow us to elucidate some aspects of the carbonate formation.

High $\delta^{18}\text{O}$ values and their minor variations along the section are evidence of substantial stability in the hydrosphere-sediment isotopic-geochemical system. One can suggest that, despite a complicated evolution of the Baltic Sea during the existence of the Baltic Glacial Lake, the hydrological regime was rather stable relative to isotope geochemistry.

It follows that variations in the isolation degree of the Baltic Sea from the World Ocean must have led to changes in salinity and chemical composition of water, and thus, to relative changes in its freshwater volume. All this should have affected the oxygen isotopy of the Baltic Sea water and precipitated carbonates. However, the obtained isotope data suggest that these processes have not resulted in any significant changes of the oxygen isotopic composition, likely owing to stagnation of bottom waters in deep depressions of the Baltic Sea.

Variations of the carbon isotopic composition along the sedimentary section are mainly caused by different contributions of isotopically heavy sedimentary (carbonate) carbon and isotopically light (oxidized) C_{org} into the sediment. This is, in turn, related to different contents of shell carbonate and C_{org} in the mud. Based on the average $\delta^{13}\text{C}$ value (-22.8‰) in OM from the recent Baltic Sea sediments (Lein *et al.*, 1986), we can suggest that 30–40% of CO_2 in studied samples is of microbial origin.

The main anaerobic oxidizer of OM in sediments at the study station is sulfate of the interstitial water. According to data by Emel'yanov *et al.* (1986), about 77% of diagenetically produced carbon dioxide is of microbial origin. However, in the case of high Mn content, its contribution into the OM oxidation rises up to 30% C_{org} (Fig. 5). The relationship between $\delta^{13}\text{C}$ and Fe is inverse (Fig. 5).

Hence, we can conclude that processes of the manganese carbonate formation in the Baltic Sea sediments were similar to those in manganese deposits of the first (diagenetic) type: Nikopol, Mangyshlak and others (Kuleshov and Dombrovskaya, 1997). The isotopic

composition of carbonates in recent Baltic Sea sediments is formed during redox diagenetic processes, as a result of chemical redistribution of elements within the sediment sequence.

Manganese sources in waters and sediments of the Baltic Sea may be different (Kuleshov and Rozanov, 1998). However, continental runoff is undoubtedly the main one. Forms of manganese delivery by rivers and its modern budget in the Baltic Basin are studied in detail by A.I. Blazhchishin, E.M. Emel'yanov, T.I. Gorshkova, I.M. Varentsov, and many other Russian and foreign authors. The results are available in their fundamental works.

Ferromanganese Nodules of the White Sea (Onega Bay)

Ferromanganese nodules are quite unevenly distributed in the Onega Bay. They are mainly concentrated within a small area of the axial depression and off the Onega coast near the Lyamtsa village. Continuous nodule fields found in this area are represented by spheroidal, discoid, and flat nodules. Ferromanganese rims on pebbles and micronodules also occur (Chistyakova, 1987). Only ferromanganese films on pebbles and rare micronodules occur within the rest of the bay area.

No specific features are observed in the internal structure of the nodules. All nodules have a nucleus surrounded by concentric layer intergrowths. One can observe structures indicative of hiatuses in the nodule growth and erosion of nodules at certain time intervals. Secondary redistribution of ferromanganese material within nodules, along fucoids disturbing the primary concentric zonation, is observed at some stations. This indicates that the process of diagenesis was not completed in previously formed nodules. Microstructures are rather common, which indicate a capture and burial of foraminiferal tests and balanus shells into the growing nodules. Remains of other organisms are more rare. These observations are especially important in the interpretation of data on carbon and oxygen isotopy in the carbonate constituent of nodules.

The mineral composition of ferromanganese nodules is rather variable. The following minerals are identified here: (1) manganese minerals (vernadite, birnessite, buserite-I, asbolan-buserite, and todorokite); (2) iron minerals (feroxyhite and hesengerite). The major mineral phases of the nodules are vernadite and feroxyhite (Chistyakova, 1987). The CO_2 content in samples is commonly negligible, and does not exceed 1–1.5%. Its occurrence forms in nodules are not exactly ascertained. Peaks of carbonate minerals are not observed in the diffraction patterns. CO_2 is likely incorporated in X-ray amorphous compounds of manganese and iron carbonates.

Data on carbon and oxygen isotopes in the ferromanganese nodules are shown in the diagram (Fig. 6). The $\delta^{13}\text{C}$ values are rather low, and vary within the lim-

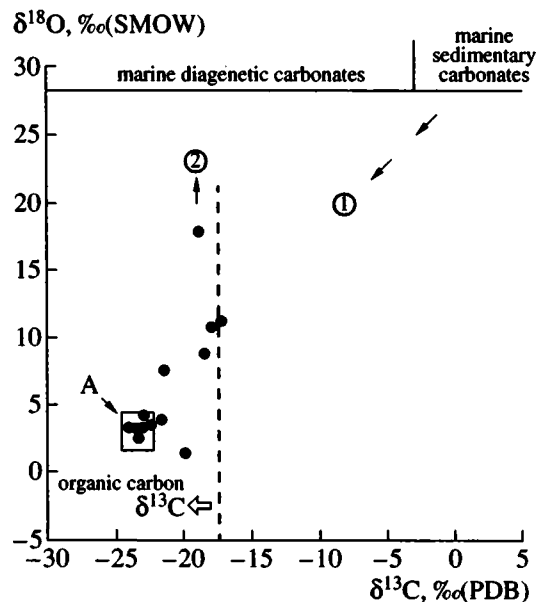


Fig. 6. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in ferromanganese nodules from the Onega Bay, White Sea (Kuleshov and Chistyakova, 1989). (A) Area of nonequilibrium diagenetic carbonates.

its from -23.5 to -17.3 ‰. The isotopic composition of oxygen is also variable. The $\delta^{18}\text{O}$ value varies within the interval from 2.5 to 17.9 ‰. As shown by Zheng *et al.* (1985), ferromanganese nodules from the North Pacific are characterized by a similar isotopic composition.

The revealed isotope relations in studied samples show that carbonate carbon in nodules is not in isotopic equilibrium with dissolved bicarbonate of the seawater. Low $\delta^{13}\text{C}$ values commonly characterize the carbon of organic origin (Kodina and Galimov, 1984). Based on this, we can confidently affirm that organic carbon participated in the formation of a carbonate constituent of ferromanganese nodules. In some cases, the carbonate in nodules is totally made up of organic carbon.

$\delta^{18}\text{O}$ values also indicate an isotopic nonequilibrium of the carbonate material with the seawater. The carbonate material is substantially enriched in light isotope ^{16}O , as compared with normal (equilibrium) sedimentary marine carbonates. Such low $\delta^{18}\text{O}$ values (up to 2 – 4 ‰) may result from C_{org} oxidation to CO_2 by manganese and iron oxides within the ferromanganese nodules. This process is also characterized by C_{org} oxidation within ferromanganese nodules in a sufficiently closed system, relative to the seawater oxygen. Because of this, the newly formed CO_2 has no time for oxygen isotope exchange with seawater, and may entirely inherit the oxygen isotopic composition of sediments.

Therefore, the carbon and oxygen isotopic composition values obtained allow us to conclude that the carbonate constituent of ferromanganese nodules from the Onega Bay, White Sea, is formed at the stage of early

diagenesis, as a result of OM oxidation by oxides of Mn and Fe (up to a carbonate form). Resulting $\delta^{13}\text{C}$ values must range about -25 to -22‰ , and those of $\delta^{18}\text{O}$ must be about 2 – 6‰ . This carbonate occupies area A in the diagram (Fig. 6).

A linear relationship is revealed in the distribution of the carbon and oxygen isotopic composition of samples studied. It results mainly from a minor admixture of sedimentary carbonate, which is in equilibrium with the seawater, in the nodules (Fig. 6, trend I). As noted above, findings of foraminiferal tests and other organic remains are direct evidence for this. However, an addition of the equilibrium carbonate is negligible, and it is almost not appreciable in some samples.

The linear relationship found may be complicated by an appearance of some samples outside the mixing line. It is quite understandable, because the diagenetic process also occurs today, and owing to this, one can find nodules without isotopic equilibrium in some cases. Sample 35/83 may serve as an example of this (Kuleshov and Chistyakova, 1989). We found residual C_{org} content here that is evidence of incomplete diagenetic OM oxidation.

The shifting of samples from the equilibrium line along the $\delta^{18}\text{O}$ axis is caused by oxygen isotope exchange of diagenetic carbonates in nodules with the seawater. This trend is shown by arrow 2 in Fig. 6.

The revealed regularity in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ distribution in the carbonate constituent of diagenetic ferromanganese nodules from the Onega Bay is not unique. It entirely corresponds to distribution patterns of carbon and oxygen isotopic composition in recent diagenetic ferromanganese precipitates from Lake Punnus Jarvi, Karjala Isthmus.

MANGANESE CARBONATES IN LACUSTRINE SEDIMENTS (EXAMPLES FROM KARJALA LAKES)

Many lakes containing ferromanganese nodules in sediments are known on the Baltic Shield, which is mainly composed of granitoids and other acidic varieties of igneous and metamorphic rocks, and also in adjacent parts of the Russian Plate. Lakes of the Karjala Isthmus, and especially Lake Punnus Jarvi (Krasnoe), are most noticeable.

Ferromanganese Nodules from Lake Punnus Jarvi

Lake Punnus Jarvi stands out among the Karjala Isthmus lakes for the best developed processes of modern ferromanganese sedimentation, expressed by the formation of oxide ferromanganese and carbonate manganese nodules in the upper layers of Holocene deposits. Because of this, many researchers working in different fields showed special interest (Semenovich, 1958; Shterenberg *et al.*, 1966, 1970; Sokolova-Dubin-

ina and Deryugina, 1962, 1967a, 1967b; Strakhov, 1965, 1976; Strakhov *et al.*, 1968; and others).

Punnus Jarvi sediments are subdivided into three groups: modern, transitional, and ancient. Modern littoral sediments, approximately to a depth of 2–4 m, consist of pebble and variegated sand. The entire clastic material in this zone is mainly represented by fragments of granitoids and less common Cambrian sandstone. Sand is most widespread in the northern part of the lake, where it covers up to 50–70-m wide zones.

Dark greenish gray liquid mud, with a considerable content of aleurite (50–53%) and sand (up to 10%), is widely developed in the central part of the lake. Black microzones and interlayers containing somewhat increased amounts of iron sulfides (mainly hydrotroilite rapidly oxidizing in the air) occur among the mud. Thickness of the mud is variable. Maximum thickness, up to 1.6 m, occurs in the central part of the basin. Transitional deposits between the nearshore sand and the deep-water mud are represented by muddy sand that differs from the more deep-water sediments by a lighter color and considerable admixture of sand and aleurite. Ancient deposits of Punnus Jarvi are represented by light gray, varved, glacial-lacustrine clay, characterized by distinct alternating "summer" and "winter" laminae.

Average contents of Mn, Fe, and C_{org} in modern and ancient Punnus Jarvi sediments are variable, and show a regular increasing trend from near-shore ones to more deep-water ones. The more ancient deposits, unlike the modern ones, are characterized by somewhat lower contents of Mn, Fe, and C_{org} . These data allow us to suggest that during the deposition of varved clay (and likely somewhat later), the metal supply into the basin was very scarce.

Shterenberg *et al.* (1970) subdivided ferromanganese ores of Lake Punnus Jarvi and other Karjala and Kola Peninsula lakes into two genetic types. Type 1 is represented by diagenetic ore. Within Lake Punnus Jarvi, this ore occurs mainly within the major ore field (Fig. 7).

The composition and structure of diagenetic ore are characterized by both lateral and vertical changes. The ore nodule size decreases (up to total disappearance) from the central part of the ore deposit towards the deep-water part of the lake. The largest nodules occur in the central part of the ore field. The ore nodules are characterized by an increased content of Mn and Ba and low contents of Fe and P. Toward the shoreline, within the closer wedge-out zone, the ore nodules lose their spheroidal shape and become flat. Within the extreme nearshore part, the ore material occurs as thin crusts and films on boulders and pebbles. The data on mineralogy of essentially diagenetic ferromanganese ore are rather incomplete up to date. According to data by different researchers, who used optical microscopy, chemical, spectral, X-ray, and other analyses, X-ray amorphous manganese and iron hydroxides, attributed

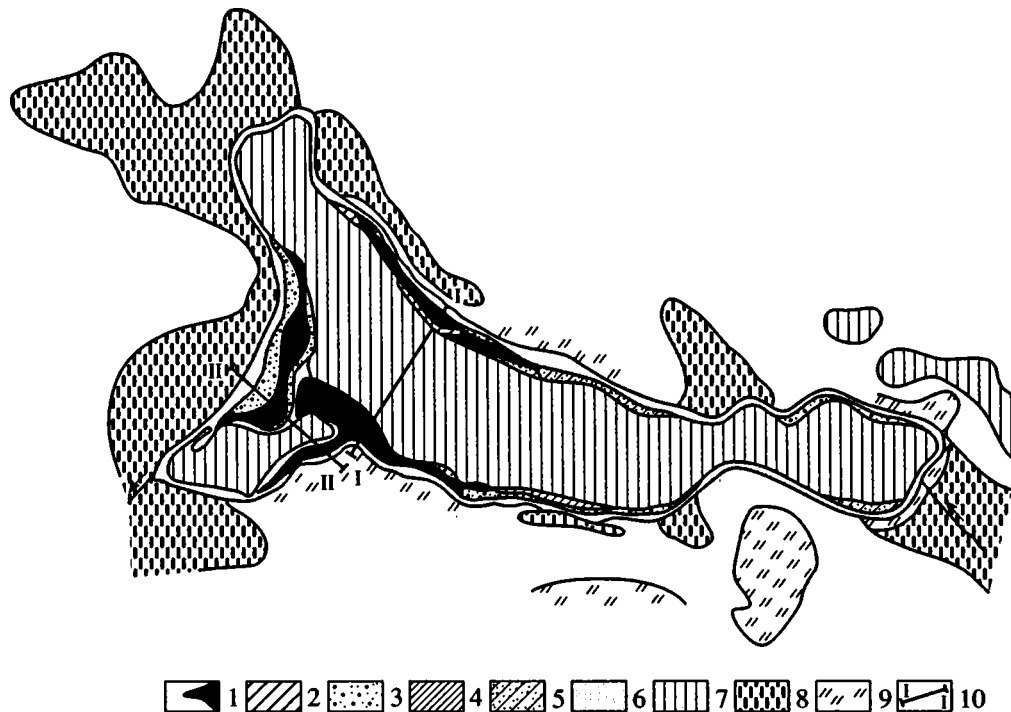


Fig. 7. Distribution of sediments and ores in Lake Punus Jarvi (Semenovich, 1958) and location of profiles where samples were collected for isotope analyses (Kuleshov and Shterenberg, 1988). (1) Ferromanganese nodule fields; ferromanganese nodules in: (2) aleurite, (3) sand; (4) varved lacustrine clay; (5) aleurite; (6) sand; (7) mud; (8) swamps without iron hydroxides; (9) peat bogs; (10) location of profiles.

today to vernadite and hydrogoethite by many authors, predominate in the Punus Jarvi ore.

Type 2 ore is considered as an essentially sedimentary ore. As a rule, it occurs in the shallow-water zone of the lake. Nodules of this type are smaller in size. The ore is rich in Fe and P, and poor in Mn and Ba. Such minerals as hydrogoethite, vivianite, and hydrofer-richlorite predominate in their composition.

The major ore field of Lake Punus Jarvi is mainly composed of diagenetic nodules. It extends, as an almost continuous elongated belt, from the Myhkyr Niemi cape to the northwest, up to the opposite coast of the lake, and is only interrupted by a narrow zone of ore-barren sediments in the deepest part of the lake (Fig. 7). In the north-eastern coastal area, as well as in other shallow-water areas, ore occurs within narrower zones among sandy deposits. The thickness of the ore bed is up to 0.20–0.22 m within the major ore field.

According to data by Strakhov *et al.* (1968), the CO₂ content in sediments is extremely low within a great majority of the lake area, and does not even exceed tenths of a percent. However, CO₂ content increases sharply, reaching values up to 2.5–3.5%, within the area of the ferromanganese ore occurrence. A pertinence of CO₂ to the ore facies is apparent here. A higher CO₂ content in sediments of the ore zone is related to the presence of mainly manganese carbonates, and lesser to iron carbonates. Such a relationship is well

demonstrated by the diagram (Fig. 8), where the CO₂ content, in ferromanganese nodules from the profile II–II', is plotted against the MnO content.

Our data (Kuleshov and Shterenberg, 1988) generally correspond to the results by previous authors

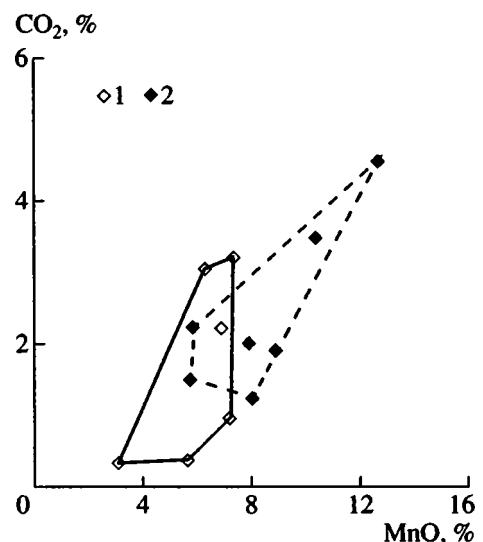


Fig. 8. Relationship between MnO and CO₂ in nodules from Lake Punus Jarvi, profile II–II'. (1) Eastern part; (2) western part.

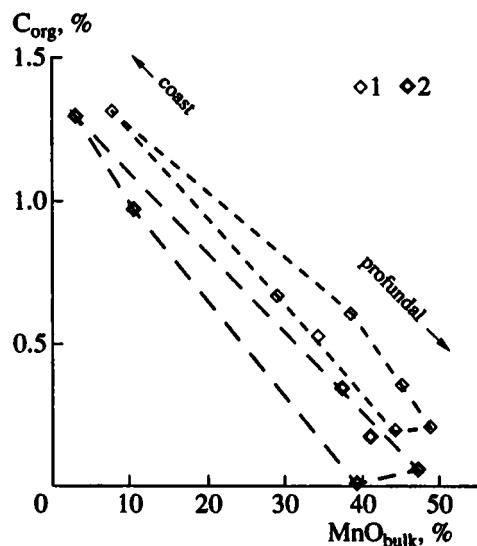


Fig. 9. Relationship between C_{org} and MnO in nodules from Lake Punnus Jarvi. Profile II-II': (1) eastern part; (2) western part.

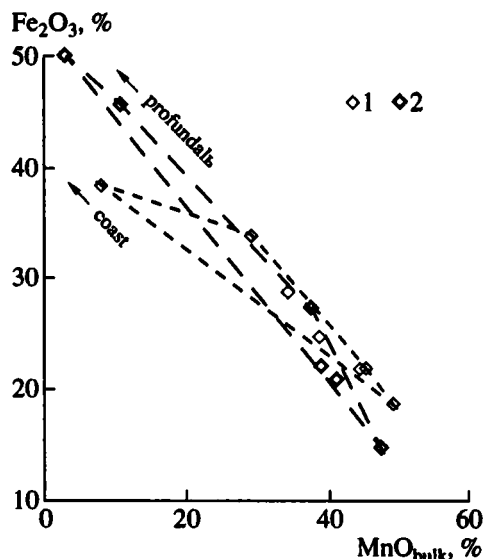


Fig. 10. Relationship between MnO and Fe_2O_3 in nodules from Lake Punnus Jarvi. For symbols see Fig. 9.

(Shterenberg *et al.*, 1970; Strakhov *et al.*, 1968). Iron and CO_2 content in the ore increases, and the Mn content decreases, with a distance from the shoreline towards deeper parts of the basin, along the eastern section of the profile II-II'. Behavior of Mn^{2+} and Mn^{4+} is identical: their concentration in the ore considerably decreases with the deepening of the basin. The CO_2 content is unevenly distributed in the ore nodules. The highest CO_2 concentration is noted within the major ore field.

Relationships between major chemical components in ore nodules are variable, and are controlled by local

conditions of ore formation. For example, some differences in CaO and MgO relations are noted between western and eastern parts of the profile II-II' studied. CaO values are somewhat higher in the eastern part of the profile.

Relations between MnO_{bulk} and C_{org} are also considerably different in these parts of the profile (Fig. 9). However, we have to note that relations between Fe_2O_3 and MnO_{bulk} are almost the same here (Fig. 10). This is possibly evidence for a common ore-forming mechanism both within the studied profile II-II' and in the ore field as a whole. A reverse trend in the distribution of Fe, Mn, and C_{org} is noted in the western part of the profile: C_{org} and Mn content increases, while the Fe content decreases towards the open part of the lake.

According to Shterenberg *et al.* (1966), the carbonate phase of the ferromanganese ore from Lake Punnus Jarvi is dominated by calcium rhodochrosite, with a minor isomorphous admixture of $CaCO_3$ and $FeCO_3$, constituting up to 7–8% of its bulk composition. Sokolova-Dubinina and Deryugina (1967) also showed that the dominating manganese carbonate in the Punnus Jarvi ferromanganese nodules is rhodochrosite.

Our study (Kuleshov and Shterenberg, 1988) supports this conclusion. X-ray diffraction results related to two samples of ferromanganese nodules collected from the major ore field are shown in Fig. 11. These data indicate a wide spectrum of carbonate minerals in the ore composition: from siderite ($FeCO_3$) with $d = 2.78 \text{ \AA}$ to siderite containing a minor isomorphous admixture of $CaCO_3$ and $MnCO_3$ to rhodochrosite ($MnCO_3$) with $d = 2.79 \text{ \AA}$, representing the main carbonate phase in the ore, and further, to a series of transitional phases between rhodochrosite and calcite (calcium rhodochrosite, manganocalcite). The isomorphous series terminates in studied nodules with calcite ($d = 3.03 \text{ \AA}$).

Isotope data and discussion. Values of $\delta^{13}C$ in the carbonate constituent of the Punnus Jarvi ferromanganese nodules vary from -28.2 to -19.2% , and those of $\delta^{18}O$ vary from 6.0 to 23.7% . These data show that $\delta^{13}C$ values are very low, as is characteristic for carbon of an organic origin. They are much lower, as compared with lacustrine carbonates precipitated in isotopic equilibrium with the bicarbonate of lake water. Mollusk shells serve as an example of the latter. $\delta^{13}C$ values for two anadonta bivalve shells from the lake are -9.5 and -8.5% ; $\delta^{18}O$ values for those are 21.5 and 21.6% , respectively. Such high $\delta^{13}C$ and $\delta^{18}O$ values, similar to those in mollusks, are characteristic for carbonates in sediments from lakes of Baltic states (Martmaa *et al.*, 1982) and from other lakes of the humid regions (Polyakov *et al.*, 1982).

Hence, decomposed organic matter of lake sediments serves as a source of CO_2 in studied ferromanganese nodules.

Dispersion of oxygen isotopic composition values in the carbonate constituent of studied samples enve-

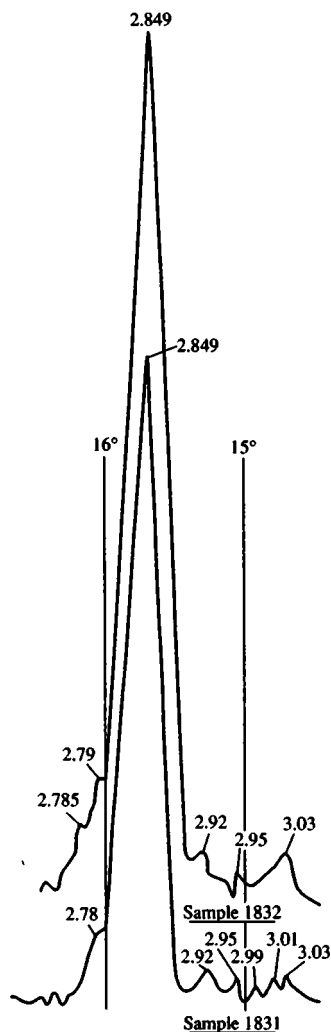


Fig. 11. X-ray diffraction patterns of carbonate-oxide ores from Lake Punnus Jarvi (Kuleshov and Shterenberg, 1988).

lopes a wide range of $\delta^{18}\text{O}$ values characteristic for carbonates, which are in isotopic equilibrium with the lake water oxygen, on the one hand, or are enriched in light isotopes that are shifted toward the oxygen of Fe and Mn oxides, on the other hand. In some cases (western part of the profile II-II'), a linear relationship is noted in distribution patterns of carbon and oxygen isotopic composition (Fig. 12).

Obviously, we can suggest that the relationship reflects a mixing line. Based on this suggestion, one can assume that initial CO_2 sources should be characterized by carbon and oxygen isotope relations that are inherent to extreme opposite areas of determined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. One of these sources must apparently be located within the area of extremely high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (area A). $\delta^{13}\text{C}$ values must range from -23 to -19‰ , while $\delta^{18}\text{O}$ values must be about 21.5‰ ; i.e., these values must be in equilibrium (or close to the equilibrium) with counterparts in the bicarbonate dissolved in interstitial waters of lake sediments. This

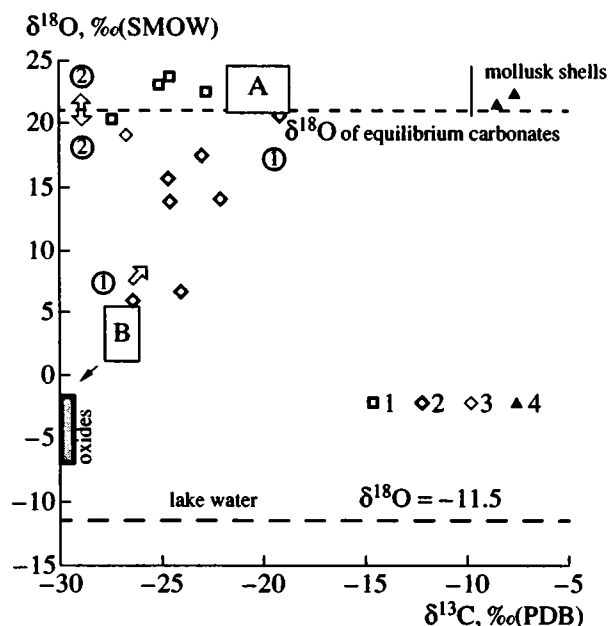


Fig. 12. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate-oxide nodules from Lake Punnus Jarvi. (A) Area of equilibrium diagenetic lacustrine carbonates; (B) area of nonequilibrium diagenetic lacustrine carbonates. (1) Profile I-I', southern part; (2) profile II-II', western part; (3) nodule from Lake Konchozero; (4) mollusk shells.

source may be arbitrarily considered as carbon dioxide of lacustrine diagenetic carbonates with the oxygen in isotopic equilibrium with lake water.

It should be noted that we do not see any marked addition from carbonates, which are in equilibrium with lake water (the isotope relationship of carbonates corresponds to that of mollusk shells). This supports, once more, the suggestion that the carbonate in ore nodules is of diagenetic origin.

The other source of CO_2 should be most enriched in light carbon and oxygen isotopes (area B). Its $\delta^{13}\text{C}$ values must likely be -25‰ or lower, while $\delta^{18}\text{O}$ values should approach those for oxygen of iron and manganese oxides (from -7 to -2‰). Among natural compounds, such a light carbon isotopic composition is commonly characteristic for some groups of organic matter (Kodina and Galimov, 1984). One can suggest that its oxidation by oxygen of iron and manganese oxides is the main source of isotopically light carbon detected in our samples.

As a rule, carbon dioxide from source B is enriched in light oxygen isotope ^{18}O (up to $\delta^{18}\text{O} = 16\text{‰}$). This value is much lower, as compared with that for carbonates in equilibrium with the lake water. Such a relationship is mainly observed in samples from the profile II-II', whereas oxygen of the carbonate constituent in the ore from profile I-I' is in isotopic equilibrium with the lake water. This possibly indicates an intensity of OM oxidation inside the ore nodules, leading to a reduction

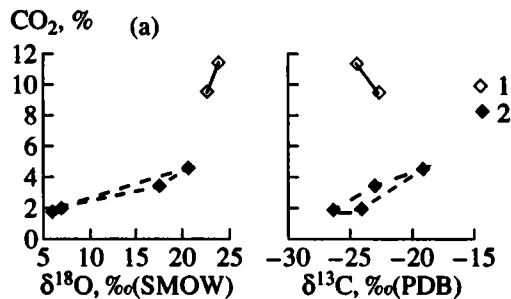


Fig. 13. Distribution of (a) $\delta^{18}\text{O}$ and (b) $\delta^{13}\text{C}$ values relative to CO_2 content in nodules from Lake Punnus Jarvi. (1) Profile I-I', southern part; (2) profile II-II', western part.

of manganese and iron oxides and to their transformation into carbonate phases.

Proceeding from the assumption about the mixing line, we can understand the correlation of carbon and oxygen isotopic composition with CO_2 content in bulk samples observed in studied profiles I-I' and II-II'. The correlation is well demonstrated for the profile II-II' (Fig. 13). As a rule, the carbonate content is directly correlated with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in CO_2 of the bulk sample.

The isotopic composition of carbon dioxide in ore nodules becomes heavier along the profile with increasing distance from the shoreline towards the profundal zone. This results from an increasing amount of isotopically balanced carbonates in samples. In the same direction, oxide nodules are replaced with oxide-carbonate ones, and in some cases even with carbonate ones.

The carbonate content is lowest in nearshore areas of the ore field, and the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are also commonly noted here. This results from an increase in the relative proportion of nonequilibrium diagenetic carbonates (B) in the carbonate constituent of nodules.

The presence of nonequilibrium carbonates in the ore nodule allows us to suggest that the oxidation of OM to CO_2 takes place inside the ore material during diagenesis (Strakhov, 1960). The CO_2 may be coupled with Mn^{2+} (more rarely with Fe^{3+}) to form carbonate minerals. Because of this, we can expect and actually find that the entire "spectrum" of isotope relationships in the carbonate part of ore nodules change from the values characteristic for equilibrium diagenetic carbonates to those inherent in isotopically nonequilibrium ones. This trend is marked by arrows (1) in the diagram (Fig. 12).

The observed relationship between manganese oxide and organic matter (Fig. 9) can also serve as evidence for such a conclusion. The highest concentrations of MnO_{bulk} , Mn^{2+} , and CaO mainly related to the carbonate phase are also observed in ore nodules with a minimum C_{org} content. This is reflected by a correla-

tion of MnO and CaO content with an isotopic composition of carbon and oxygen, as well as by the interdependence of CaO and MnO concentration values.

Meanwhile, another trend in the distribution of $\delta^{18}\text{O}$ values is also noted in the formation of carbonates from CO_2 produced by OM oxidation within ore nodules. It consists in approaching the equilibrium between lake water and newly formed carbonates in oxygen isotopy. The carbon isotopic composition remains the same in this process, i.e., carbon is isotopically light, but oxygen becomes isotopically heavier. This trend is marked by arrows (2) in the diagram (Fig. 12).

Aside from the processes considered above, we have to take into account one more process rather widely developed in diagenetic conditions: the OM oxidation owing to sulfate reduction. In this case, the produced CO_2 would be enriched in light oxygen isotope showing $\delta^{18}\text{O}$ values from 2 to 10‰, close to those of sulfate oxygen (Claypool *et al.*, 1980; Grinenko *et al.*, 1986; Pierre and Rouchi, 1986).

Therefore, all variations in carbon and oxygen isotopy revealed in studied samples mainly result from the above mentioned reasons. Minor changes in pH values of sediments in the lake and within the ore field, as well as variations in Eh values (Sokolova, 1962), do not affect the distribution of $\delta^{13}\text{C}$ values in our samples (Ohmoto, 1972; Thode *et al.*, 1965).

The isotope data obtained, support the conclusion by previous researchers regarding the diagenetic origin of ore nodules and their carbonate constituent, in particular. In general, we support ideas about geochemistry and behavior of elements in diagenetic processes, which were perfectly described in fundamental works by Strakhov (Strakhov, 1960, 1965, 1976; Strakhov *et al.*, 1968) and by many of his followers.

Thus, the carbonate constituent in the Punnus Jarvi ore nodules (and likely in many other Karjala lakes) is represented by two generations differing in isotopic composition: (a) type 1, which is in isotopic equilibrium with lake water, relative to oxygen, and characterized by high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values; and (b) type 2, which is in isotopic nonequilibrium and characterized by a lighter isotopic composition of carbon and oxygen. The latter is formed owing to OM oxidation inside ore nodules. Proper sedimentary lacustrine carbonates in isotopic equilibrium with the lake water bicarbonate were not found in the ore nodules.

ISOTOPE GEOCHEMISTRY OF MANGANESE CARBONATE FORMATION IN RECENT SEDIMENTS

In order to reveal regularities in the formation of manganese carbonates in recent sediments and their isotopic composition, we examined a wide range of manganese carbonates formed in quite different sedimentary environments: oceanic, marine, and lacustrine. By choosing the study objects, we tried to exclude the

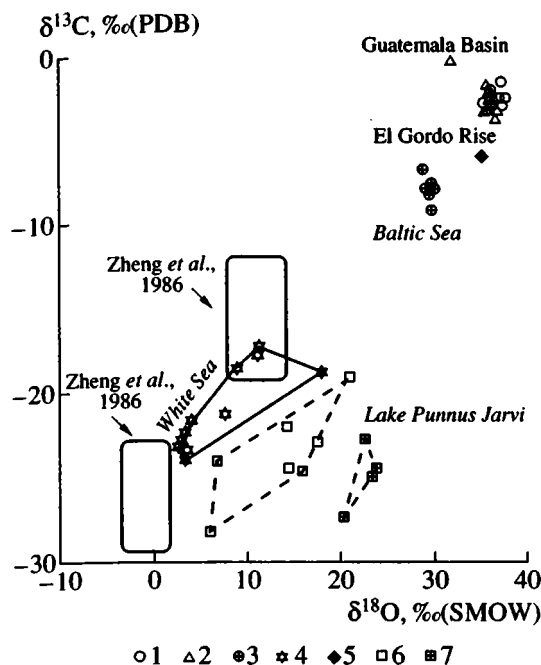


Fig. 14. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in manganese carbonates from recent sediments. (1) Guatemala Basin, Pacific Ocean; (2) Guatemala Basin, Pacific Ocean, data from (Coleman *et al.*, 1982); (3) Gotland Deep, Baltic Sea; (4) Onega Bay, White Sea; (5) El Gordo Rise, Middle America Trench, Pacific Ocean; (6, 7) Lake Punnus Jarvi, Karjala Isthmus: (6) profile II-II', western part; (7) profile I-I', southern part.

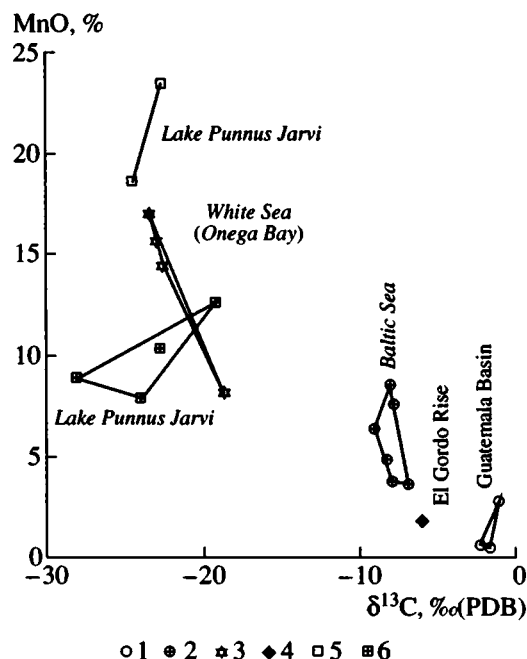


Fig. 15. Relationship between $\delta^{13}\text{C}$ values and MnO content in manganese carbonates from recent sediments. (1) Guatemala Basin, Pacific Ocean; (2) Gotland Deep, Baltic Sea; (3) Onega Bay, White Sea; (4) El Gordo Rise, Middle America Trench, Pacific Ocean; Lake Punnus Jarvi, Karjala Isthmus: (5) profile I-I', southern part, (6) profile II-II', western part.

regions where modern hydrothermal processes significantly affect normal sedimentary processes. Because of this, our interpretation of geochemical and isotope data does not take into account the influence of hydrothermal (and volcanic) processes in formation of the isotopic composition of authigenic manganese carbonates.

The isotope data considered above confirm the existing idea about the diagenetic origin of manganese carbonates in lacustrine, marine, and oceanic sediments. They allowed us to elucidate some aspects of their formation in more detail and to ascertain general regularities in the geochemistry of carbon and oxygen isotopes in these processes. All isotope data considered in this paper are presented in Fig. 14, in coordinates $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$. It is well visible that manganese carbonates in sediments from various types of basins occupy different fields. Fields of ferromanganese oxide nodules from the Onega Bay (White Sea), and nodules from Lake Punnus Jarvi, with the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are located in the lower left side of the diagram, whereas plots of rhodochrosite from the Guatemala Basin sediments (Pacific Ocean), with the heaviest isotopic composition, fall into the upper right side. Manganese carbonates from deep-water sediments of the Baltic Sea occupy an intermediate position.

Such a distribution of isotope relationships is controlled by one, likely, crucial factor: the degree of OM

contribution (more exactly, a contribution of carbon dioxide of microbial origin generated within a sediment as a result of OM oxidation) in the process of authigenic manganese carbonate formation during diagenesis. Finally, this distribution pattern is controlled by the initial C_{org} content in sediments and by its activity in the diagenetic zone. $\delta^{13}\text{C}$ values may indicate a relative proportion of organic or sedimentary carbon dioxide in the composition of studied carbonates. So, we observe the highest content of carbon dioxide, formed due to C_{org} oxidation, in lacustrine carbonates and in the carbonate constituent of ferromanganese nodules, whereas its content is the lowest in oceanic sediments.

The mechanism of the influence of organic matter on manganese accumulation in diagenetic processes, and its forms are discussed in detail in fundamental works by Strakhov and his followers (Shterenberg, 1975; Strakhov *et al.*, 1968; and others).

The conclusion on the crucial role of organic matter in diagenetic manganese carbonate formation is well confirmed by the observed relationship between $\delta^{13}\text{C}$ values and MnO content in studied manganese carbonates (Fig. 15). In general, it is ascertained that the higher the manganese concentration in sediments, the lighter the isotopic composition of carbon, i.e., more microbial CO_2 is included into manganese carbonates. The same relationship is also observed in carbonate

manganese ores of well known manganese deposits, such as Chiatura and Kvirili (Kuleshov and Dombrovskaya, 1997), Nikopol (Kuleshov and Dombrovskaya, 1988), Usa (unpublished data by the author), and several others.

The available isotope data show that manganese carbonates in recent sediments are formed during diagenesis, with more or less active participation of carbon released from decomposed organic matter. Proper sedimentary manganese carbonates, which are directly precipitated from the water column as a result of chemical or organogenic precipitation and, hence, are in isotopic equilibrium with dissolved bicarbonate of the sedimentary basin, have not been found up to date. Because of this, it is likely necessary to introduce corrections into the upwelling hypothesis of sedimentary manganese deposit formations proposed by Sapozhnikov (1967). It is assumed that the precipitation of Mn from Mn-rich deep waters flowing into the coastal zone (coastal upwelling) likely occurred only in oxide form. Judging by available isotope data on recent deposits and carbonate manganese ores from several deposits (Kuleshov and Dombrovskaya, 1993), manganese carbonates could not be formed by this mechanism.

We would like to pay special attention to carbonates in ferromanganese oxide concretions and nodules. These carbonates likely represent a specific type of diagenetic manganese carbonates. They are likely formed as a result of OM oxidation inside nodules, by both the oxygen of the sediments themselves, and mainly, the oxygen of manganese oxides. The possibility of such a carbonate formation was noted by Varentsov *et al.* (1973, 1977) for ferromanganese nodules from the Baltic Sea. $\delta^{13}\text{C}$ values in such carbonates correspond to the isotopic composition of initial organic matter, whereas $\delta^{18}\text{O}$ values are controlled by oxygen of sediments themselves.

Two groups are distinguished in this type of carbonate, according to their isotopy. Group 1 represents the "youngest" type carbonate that is presently formed within nodules. Its oxygen isotopic composition is determined by the oxygen isotopy of oxides, and is characterized by the lowest $\delta^{18}\text{O}$ values (3–5‰ for the Onega Bay nodules; 6‰ and less for those of Lake Punnus Jarvi).

The isotopic composition of these carbonates becomes heavier with time, due to the oxygen isotope exchange with basin water (marine or lake), and reaches an isotope equilibrium with the basin water oxygen. In this case, the carbonate does not differ from diagenetic carbonates of the sediment in its isotopic characteristics. These are carbonates of group 2.

In real observations, we see the entire series of carbonate transitions from group 1 to group 2 both in the Punnus Jarvi samples (Fig. 12) and in samples from the Onega Bay (Fig. 6).

Therefore, comparing the isotope data for diagenetic carbonates from recent sediments with analogous

data for the Oligocene and older manganese deposits, we can conclude that carbonate manganese ores best correspond to carbonates from sediments of intracontinental seas in their isotopic characteristics. Proper oceanic sediments are likely not prospective for the accumulation of diagenetic manganese carbonate ores. Lacustrine manganese ores are also of low practical interest. The lacustrine ore formation, interesting for us only from a scientific point of view, as it allows us to observe in detail different aspects of the modern ferromanganese ore formation.

Discussion of manganese sources deviates from the theme of this paper. Continental runoff is apparently the main source in all basin types. However, in some regions of the World Ocean with modern hydrothermal activity and volcanism, these processes can make a considerable contribution to the metal potential of marine sediments (e.g., in the Red Sea).

Meanwhile, the hypothesis about an elision source of Mn for some large deposits has been intensely developed during recent years (Kuleshov and Dombrovskaya, 1997; Pavlov and Dombrovskaya, 1993; *Paragenesis* ..., 1990). In this connection, we believe that a possibility of manganese influx with elision waters into some sedimentary basins (mainly into marginal and intracontinental ones, for example, into the Baltic Sea) cannot be excluded.

CONCLUSION

The isotope data for the authigenic manganese and Mn-bearing carbonates from recent sediments of various basin types (oceanic, marine, lacustrine) considered above, and their distribution patterns allow us to draw the following conclusions.

(1) Authigenic manganese carbonates are formed during diagenesis with an active contribution of microbial carbon dioxide that is generated in sediments as a result of OM oxidation. Isotope data entirely confirm the ideas by N.M. Strakhov and his followers about the substantial role of organic matter in diagenetic processes, including carbonate manganese ore formation.

(2) Proper sedimentary manganese carbonates, which precipitated in isotopic equilibrium with seawater by either a chemical or biogenic mechanism are not found up to date. Based on isotope data, all manganese carbonates, both from recent sediments and ancient deposits (manganese ore deposits), are of a diagenetic origin.

(3) From the isotope-geochemical point of view, diagenetic manganese carbonates are represented in recent sediments by two types: isotopically equilibrium and isotopically nonequilibrium (in terms of the oxygen isotope equilibrium with seawater). The nonequilibrium carbonates are formed within nodules, crusts, and other morphological types of oxide aggregates, due to oxidation of organic carbon by the oxygen of manga-

nese and iron oxides. Iron carbonates formed in the same way can also be attributed to this type.

(4) Correlation between carbon isotopic composition and Mn content in sediments is revealed. It indicates a crucial role of the intensity of OM oxidation in an enrichment of authigenic carbonates with Mn. Details of the enrichment mechanism, as well as geological and geochemical conditions of this process, need further study.

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Facies and Genesis of Phosphorites from Karatau: Communication 2: Genesis of Phosphate Pellets and General Evolution of the Tommotian Paleobasin

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Abstract—The morphology of phosphate pellets from the upper phosphate bed of the Karatau basin and the genetic relation of phosphate–siliceous microfossils, pellets, and oncolites are considered. It is demonstrated that pellets were initially composed of carbonate material, which was subsequently replaced by phosphate and silica. Different stages of interaction of H₂S- and O₂-bearing facies in the Lesser Karatau are defined, and a mechanism of the phosphorite pellet formation is discussed.

MORPHOLOGY OF PHOSPHATE PELLETS FROM THE UPPER PHOSPHATE BED OF THE PROFILE

Three representative thin sections of samples from the upper phosphorite bed of the Koksuy (thin section 700), Kistas (thin section 134), and Berkuty Severnyi (thin section 1017) areas yielded different types of phosphate pellets; their distribution and dimensions are demonstrated by circular diagrams (Fig. 1).

When studying the morphology of phosphate pellets in thin sections, the following procedure was applied. In the thin section from the Koksuy locality, 2121 measurements of the maximum diameter of different-type pellets were carried out in the area of 1 cm² where phosphate pellets were typified, their average sizes were determined, and their relative distribution (in %) was estimated. The same measurements and calculations were performed in the area of 0.25 mm² in transparent thin sections from the Kistas and Berkuty Severnyi localities (168 and 508 measurements, respectively).

It appeared that 19 morphological types of pellets can be defined in phosphorites from the upper phosphate bed of the Koksuy deposit; their forms are shown in the upper circular diagram (Fig. 1a).

It was established that phosphate pellets of the simplest (oval, lenticular or rhomboidal) forms are characterized by a maximum distribution (occurrence frequency 46.9%). Less common are spherical (10.6%), tear-shaped (9.2%), triangular (7%), clavate (6.2%), prismatic (4.8%), triangular-oval (3.9%), and dumbbell-like (3.5%) pellets. Pellets with a complex structure (types 12–19) are sharply subordinate (Kholodov and Paul, 1995b).

It is interesting to note that the average size of phosphate pellets from the upper phosphate bed of the Koksuy deposit is inversely related to their distribution.

In other words, the greater the phosphate pellets (in size), the lower their occurrence frequency in phosphorites of the considered area.

In the shallower-water Kistas section (thin section 134), the number of defined pellet types is generally retained, but the proportion between simple and complex pellets slightly changes: the relative content of simple forms decreases, whereas that of complex forms increases (Fig. 1b). Moreover, the average size of some simple phosphate pellets also increases and, thus, morphometric differences between simple and complex phosphate particles disappear.

Phosphate pellets from the Kistas area are particularly characterized by a presence of large fragments of phosphate bacterial–algal mats with a complex inner structure and abundant inclusions of simpler rounded phosphate pellets; their size ranges between 532 and 916 μm averaging 726 μm (Fig. 1b). Besides, common in the considered area are “reticulate phosphorites,” i.e., rock areas composed of equidimensional, oval or ellipsoidal pellets, separated by common slightly crystallized thin envelopes with poikilitic extinction under crossed nicols.

In the Berkuty Severnyi section marking the shallowest deposition setting (Fig. 1c), the morphological diversity of phosphate pellets noticeably increases; there are 21 types of different phosphate aggregates, many of which are characterized by a complex structure.

The proportion between simple and complex phosphate pellets in this area also very strongly differs from that of the Koksuy deposit, but it is almost equal to the ratio between different pellets in the Kistas locality. Phosphate particles with the most complex morphology have maximum dimensions. In addition, this area is characterized by the presence of large phosphate oncolites (diameter from 346 to 662 μm) with abundant

phosphate fringes (Fig. 1c, 18), oncolite-like oval pellets (292 to 462 μm) with a wide algal rim (Fig. 1c, 15), abundant fragments of phosphate bacterial-algal mats (65 to 130 μm) with a complex internal structure (Fig. 1c, 21), and structureless fragments of bacterial-algal mats from 62 to 1001 m across (Fig. 1b, 20).

Demonstrated diagrams (Fig. 1) allow the problem about the role of edaphogenic processes in the phosphate pellet formation to be solved.

It is well known that the upper phosphorite member was formed under frequent and prolonged periods of reworking of muddy deposits. Hence, many phosphate particles can represent typical intraclasts, i.e., aggregates that resulted from the mechanical destruction and redeposition of initial phosphate accumulations. A great importance of mechanical redeposition in the phosphate pellet formation was emphasized in different works (Tushina, 1964; Cherbyanova, 1977; Kholodov, 1987; Eganov, 1988). This is explained to a large extent by abundant finds of fragments of phosphate rocks and breccias in the lower parts of phosphate beds.

To recognize intraclastic aggregates amid phosphate pellets, relationships between external contours of particles and their internal structure should be established. Consequent relationships between the external boundary and the internal structure are the main feature of intraclasts. On the contrary, concordant relationships are atypical of the mechanical destruction and redeposition process.

The analysis of phosphate pellet types from the upper phosphate bed unambiguously indicates an insignificant role of mechanical processes in their formation. For instance, only 2.5% of the studied pellets from the Koksui, 15% from the Kistas, and 17% from the Berkuty Severnyi deposits can be referred to as intraclasts.

Although the total amount of intraclasts noticeably increases toward shoals, they generally do not play a significant role in the formation of phosphate particles.

GENETIC RELATIONSHIPS BETWEEN PHOSPHATE-SILICEOUS MICROFOSSILS, PELLETS, AND ONCOLITES

In the first communication of this work (Kholodov and Paul, 1999), we mentioned that small phosphate and phosphate-siliceous pellets associate with phosphate-siliceous microfossils in the lower phosphorite-bearing member and underlying phosphate-siliceous rocks.

Sergeev (1992) described diverse spiral-cylindrical, tubular, and spherical coccolidal microfossils. Abundant among them are spiral-cylindrical phosphate and phosphate-siliceous microfossils of the genus *Obruchevella* Reittl. This genus is represented by four species, most important among which are *O. parva* Reittl. and *O. cf. meishucunensis* Song. The first species is usually represented by tubular hollow bodies coiled into cylindrical

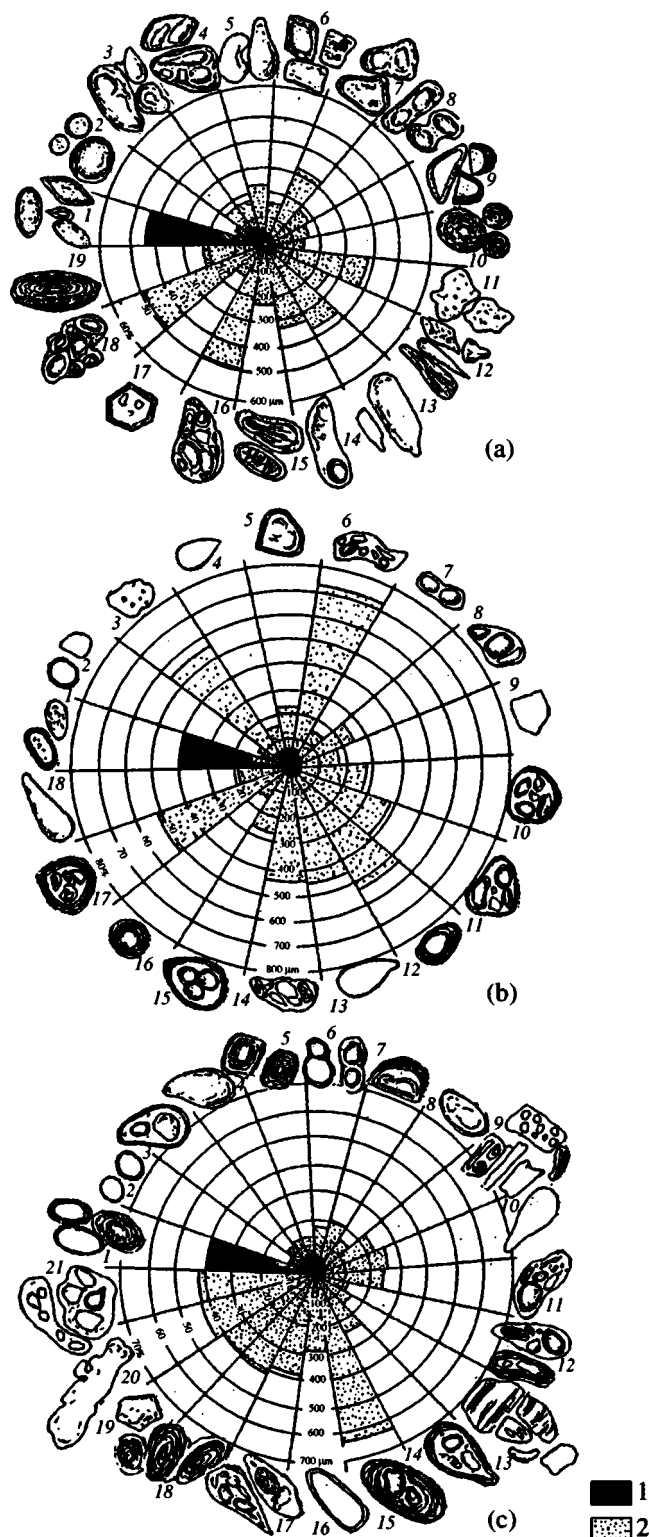


Fig. 1. Types of phosphate pellets, their distribution and dimensions. (a) Koksui; (b) Kistas; (c) Berkuty Severnyi. (1) Distribution of phosphate pellets of the different types, %; (2) average sizes of different-type pellets; (1-21) pellet varieties.

spires. The outer diameter of cylinders is 25–35 μm , whereas the inner one is 10–20 μm ; the wall thickness does not exceed 6–10 μm . The total length of the spire can reach 150–300 μm . The second species is characterized by larger dimensions of the spire: the outer diameter ranges from 120 to 130 μm , the inner one, from 105 to 115 μm , and the wall thickness amounts to 20–22 μm .

In the opinion of Sergeev, the *Obruchevella* genus microfossils prevailing in the Chulaktau assemblage, represent remnants of Cyanophyceae algae of the *Spirulina* type. A portion of them are probably fragments of destroyed bacterial–algal mats.

The phosphorite-bearing formation encloses abundant tubular *Eomecetopsis robusta* Sch. emend. Knoll et Gol. Their length amounts to 300 μm and diameter varies from 2 to 4.5 μm . Present are also similar hollow envelopes of *Siphonophycus* sp. with thicknesses ranging from 0.6 to 12 μm and lengths amounting to 330 μm . Sergeev (1992) believes that filamentous envelopes represent remnants of one or several species of oscillatorioid cyanobacteria.

Finally, coccoidal phosphate–siliceous microfossils in the Chulaktau Formation are represented by spherical *Eoentophysalis* sp., *Tetraphycus amplus* Golovenok et Belova, and *Tetraphycus acutus* Serg. Their colonies are usually characterized by nodular, spherical or ellipsoidal forms; the diameter of spheroids varies from 8–15 to 11–22 μm . Some varieties form accumulations with a common fringe; the diameter of such complex aggregates can amount to 60–70 μm . It is assumed that Tommotian coccoidal microfossils represent an analogue of modern Cyanophicaceae algae of the *Gloeocapsa* genus.

The aforesaid allows the conclusion that the boundary between phosphate–siliceous microfossils and phosphate–siliceous pellets is quite arbitrary. It is evident that only a small portion of spiral–cylindrical, tubular, and coccoidal microfossils can be determined under the microscope. Most of them, represented in thin sections by atypical slices or poorly preserved remnants, are classed with pellets and only slightly differ from the most important constituents of phosphorite beds.

It can be assumed with a high degree of confidence that the boundary between phosphate–siliceous microfossils and similar (in composition) phosphate–siliceous pellets is at 60–80 μm .

It should be emphasized that some morphometric regularities typical of phosphate pellets from the Koksu deposit are also characteristic of phosphate–siliceous microfossils (Kholodov and Paul, 1995b, 1996, 1999). This is first evident from histograms of coccoidal phosphate–siliceous microfossils from the Chulaktau and Chichkan formations of the Lesser Karatau compiled by V.N. Sergeev. Similarities in morphology and granulometric regularities of phosphate pellets and microfossils suggest their common biogenic origin.

When an amount and dimensions of algal fringes increase, pellets gradually pass into calcareous–siliceous–phosphate oncolites that are widespread in those sections, where the Chulaktau phosphorite-bearing rocks are reduced in thickness. They represent usually bacterial–algal nodules, whose peripheral part is mostly composed of a dolomitic substance, which is sometimes replaced by variable combinations of phosphate, silica, and even iron and manganese hydroxides (Fig. 2). Owing to the occurrence of hydroxides, the phosphate bed with oncolites is sometimes mistaken by geologists for a ferromanganese horizon.

It should be emphasized that it is often difficult to discriminate between multilayer phosphate pellets and phosphate–siliceous–carbonate oncolites. The boundary between them can be conventionally outlined using diagrams of size increment rates of phosphate particles (Kholodov and Paul, 1999; Figs. 7, 8). An increase in the particle increment rate begins, almost always, at a level of 400–420 μm . It seems that precisely this level can be considered as a basis for the classification boundary, and bacterial–algal nodules whose diameter exceeds 400–420 μm should be referred to phosphate oncolites. It goes without saying that, in this case, the bacterial–algal fringe should be expressed sufficiently well.

Thus, phosphate pellets represent aggregates, whose dimensions vary approximately from 60–80 to 400–420 μm . They show gradual transitions to microfossils and oncolites, and most of them probably represent bacterial–algal microcolonies. Phosphate pellets also include authigenic phosphate oolites and spherulites, although the relative amount of the latter is insignificant (Smirnov and Tushina, 1962; Litvinova, 1990), and their formation is related to later diagenetic redistribution of phosphate in muddy sediments.

The direct evidence favoring the bacterial–algal origin of some groups of phosphate pellets from the Chulaktau Formation was presented in the works by Mirtov *et al.*, (1987) and Rozanov and Zhegallo (1989). Using the scanning electron microscope, they discovered in phosphorite samples (pretreated in acids) various bacteriomorphic structures, different-type bacterial mats, fragments of cyanobacterial filaments, and also microphytolites, which served as material for phosphate particle formation. Subsequently, Shkol'nikov *et al.* (1992) established a similar bacteroid structure for phosphate pellets from the Permian Phosphoria Formation (USA).

INITIAL COMPOSITION OF PHOSPHATE PELLETS

The comparison of textures of carbonate and phosphate rocks suggests that they contain oncolites and pellets, which are completely identical in morphology.

Figure 3 demonstrates peculiarities of the texture of carbonate and phosphate oncolites. Figure 3a shows a

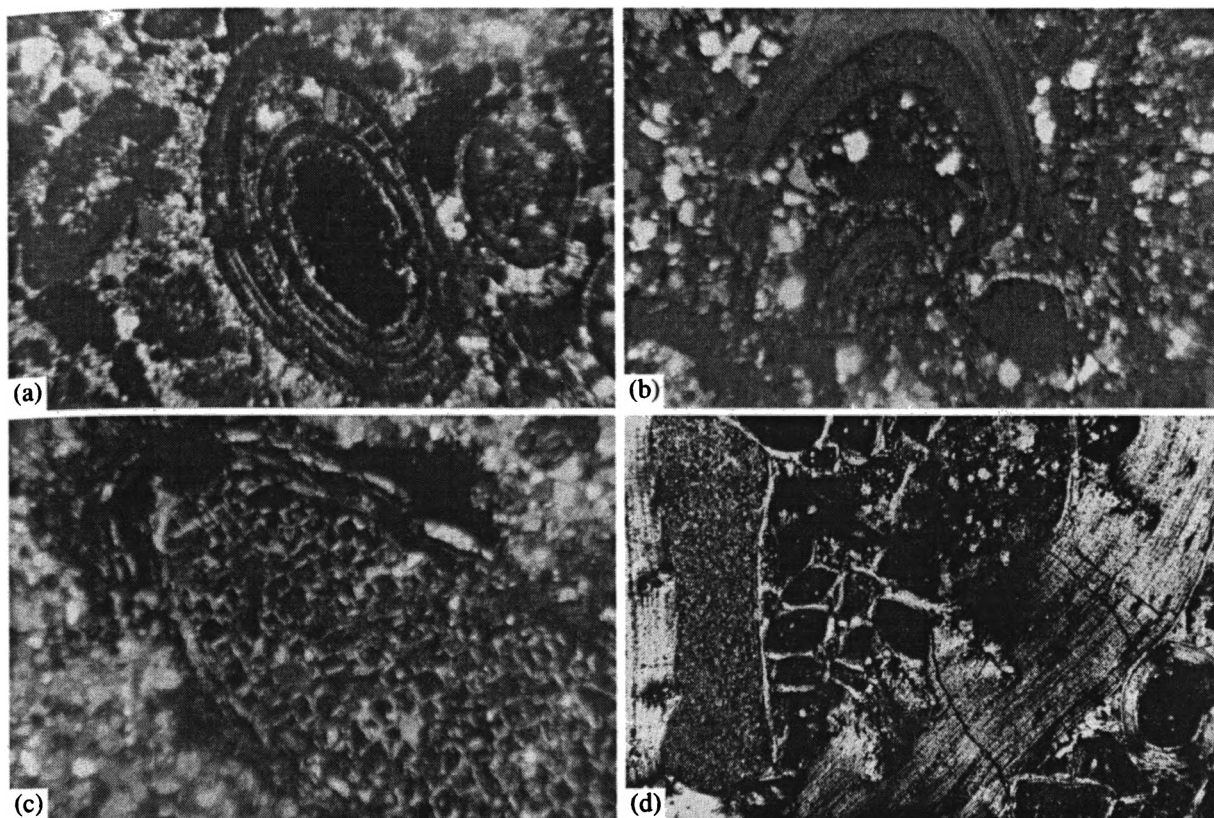


Fig. 2. Textures and structures of carbonate-siliceous-phosphate oncolites. (a) Phosphate-carbonate-siliceous oncolite, Sample 2635, Berkuty ore occurrence, magn. 50, crossed nicols. Algal fringes of variable composition envelope phosphate aggregate (black sector corresponds to phosphate; light sector is carbonate (dolomite); the broad part of the fringe encloses quartz clasts and small phosphate pellets. (b) Siliceous-phosphate oncolite, Sample 2635, Berkuty ore occurrence, magn. 50, crossed nicols. Large fragment of siliceous-phosphate oncolite within the terrigenous-phosphate cement (black sector corresponds to phosphate; gray sector is phosphate-siliceous part of the fringe (dolomite); and white inclusions depict clastic quartz). (c) Carbonate-ferruginous-phosphate oncolite, Sample 5195, Kyrchabakty ore occurrence, magn. 50, crossed nicols. The oncolite core contains reticulate phosphorites; the algal fringe is composed by dolomite (light), iron and manganese hydroxides (dark). (d) Ferruginous-manganese-carbonate oncolite, Sample 2783, Dzhiban ore occurrence, magn. 50, crossed nicols. A large oncolite with the carbonate fringe (white) and laminae of iron and manganese hydroxides (black).

photomicrograph of oncolitic dolomite from the Precambrian Kolosovo Formation of the eastern Taimyr Peninsula. According to determinations by Mil'shtein (1963), carbonate oncolites are referred to the subgroup *Osagia tenuilamellata* Reith. It is evident that the sample encloses an abundance of simple and complex bacterial-algal aggregates composed of pelitomorphous dolomite. The rock is cemented by dolomite of three generations: dolomite I cements oncolitic inclusions (a), dolomite II forms incrustate fringes around the inclusions (b), and dolomite III fills remaining pores in the rock (c).

Figure 3b demonstrates sketches of phosphate oncolites from the Chulaktau Formation (scale as for Mil'shtein's photomicrographs). Noteworthy is an amazing morphological similarity of all oncolites, which allows for the assumption that phosphate oncolites also belong to the *Osagia* genus.

It should be emphasized that in the first case, we deal with calcareous bacterial-algal structures, whereas in the second case with phosphate aggregates.

Pelletal limestone and dolomite are widespread in the Precambrian and Phanerozoic. Because of the uncertain position of this rock group, it is sufficiently difficult to define complete morphological analogues of pelletal phosphorites.

It is safe to agree with the statement by G.I. Ershova and V.L. Librovich, who wrote, with the support of works (Shvetsov, 1958; Khvorova, 1958; Folk, 1959; Maslov, 1973; and others): "...it should be taken into consideration that no unequivocal criteria for discriminating coprolites from clots, and some algal aggregates yet exist. Therefore, different researchers often refer extremely similar limestone types to coprolitic, clotty, or algal rocks" (Ershova and Librovich, 1969, p. 90). When keeping in mind that the boundary between biogenic and chemogenic carbonate allochems is almost indistinguishable, it becomes clear that pelletal

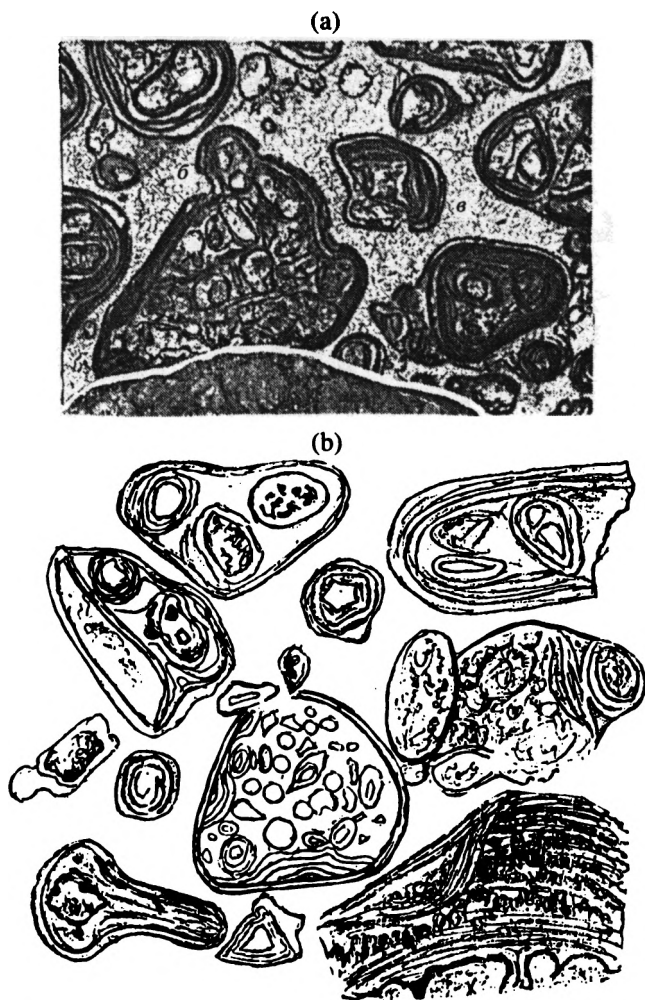


Fig. 3. Morphological types of (a) carbonate and (b) phosphate oncolites. (a) Oncolitic dolomite, photomicrograph, magn. 13, parallel nicols. Carbonate oncolites are cemented by the crystalline carbonate cement of three generations. Upper Cambrian, Kolosovo Formation, eastern Taimyr. Collection by V.E. Mil'shtein (1963); (b) sketches of photomicrographs of phosphate oncolites from sections of the studied profile in Lesser Karatau. Magn. 13.

rocks represent an extremely unfavorable object for any comparison.

However, the task is simplified by the fact that some phosphorite-bearing formations host, along with phosphate pellets, also carbonate ones similar to the latter.

For instance, Emigh (1958) was the first to describe carbonate pellets widespread in the lower phosphorite-bearing member of the Permian Phosphoria Formation (USA). Moreover, this researcher discovered different stages of the replacement of carbonate by phosphate and suggested that phosphate pellets from other productive beds most commonly represent a result of a complete replacement, when relic carbonate structures are not preserved.

Emigh's investigations were continued by works of Campbell (1962), who discovered pelletal dolomites in the Phosphoria Formation in northern Wyoming. Photomicrographs published by the latter researcher indicate a complete similarity between phosphate and carbonate allochems.

Later, Bushinskii (1966) described dolomite and phosphate pellets, as well as transitional forms from the Sinian and Lower Cambrian phosphorite-bearing successions of the Sinan depression (China). This researcher also suggested the existence of metasomatically altered phosphate pellets in Cambrian phosphorites of Karatau.

To test the hypothesis that phosphate pellets from the Chulaktau Formation of the Lesser Karatau have a complex composition, we carried out a detailed sampling of its lower and upper parts in different areas of the studied profile. It appeared that transitions between both the Berkuty dolomites and the Chulaktau Formation, between the Chulaktau Formation, and overlying Tamda carbonate rocks (Shabakta Formation), represent areas of co-existence for carbonate and phosphate pellets.

The fact that form and dimension in pellets of variable compositions correspond to each other, i.e., every phosphate pellet that has its complete carbonate analogue, is of interest. Figure 4 illustrates the comparison of structural peculiarities and the composition of phosphate and carbonate pellets from transitional zones.

It is seen that these two different mineralogical varieties contain round (a, b), oval (c, d), dumbbell-like (e, f), tear-shaped (g, h, j), pear-shaped (i, k), and complex oncolite-like structures. One can state that the entire morphological diversity of phosphate pellets is completely repeated in carbonate varieties.

Curiously, however, phosphate particles usually preserve all details of the pellet's internal structure (external fringes, texture of separate complex grains, and others), whereas in carbonate pellets, all these features are eliminated.

This allows the assumption that the complex internal structure of carbonate pellets can be explained by the secondary recrystallization of carbonate material; a prolonged crystallochemical history of carbonate rocks did not favor the preservation of initial textures in the latter.

It should also be emphasized that carbonate pellets noticeably differ from phosphate pellets usually by the presence of a significant amount of dispersed and impregnated organic matter.

The detailed study of carbonate pellets also revealed an extreme mineralogical heterogeneity in their composition (Fig. 5). Against the background of a relatively uniform carbonate substance, the pellets frequently include areas of secondary phosphatization and silicification; sometimes, relics of primary dispersed organic matter are preserved within the grains.

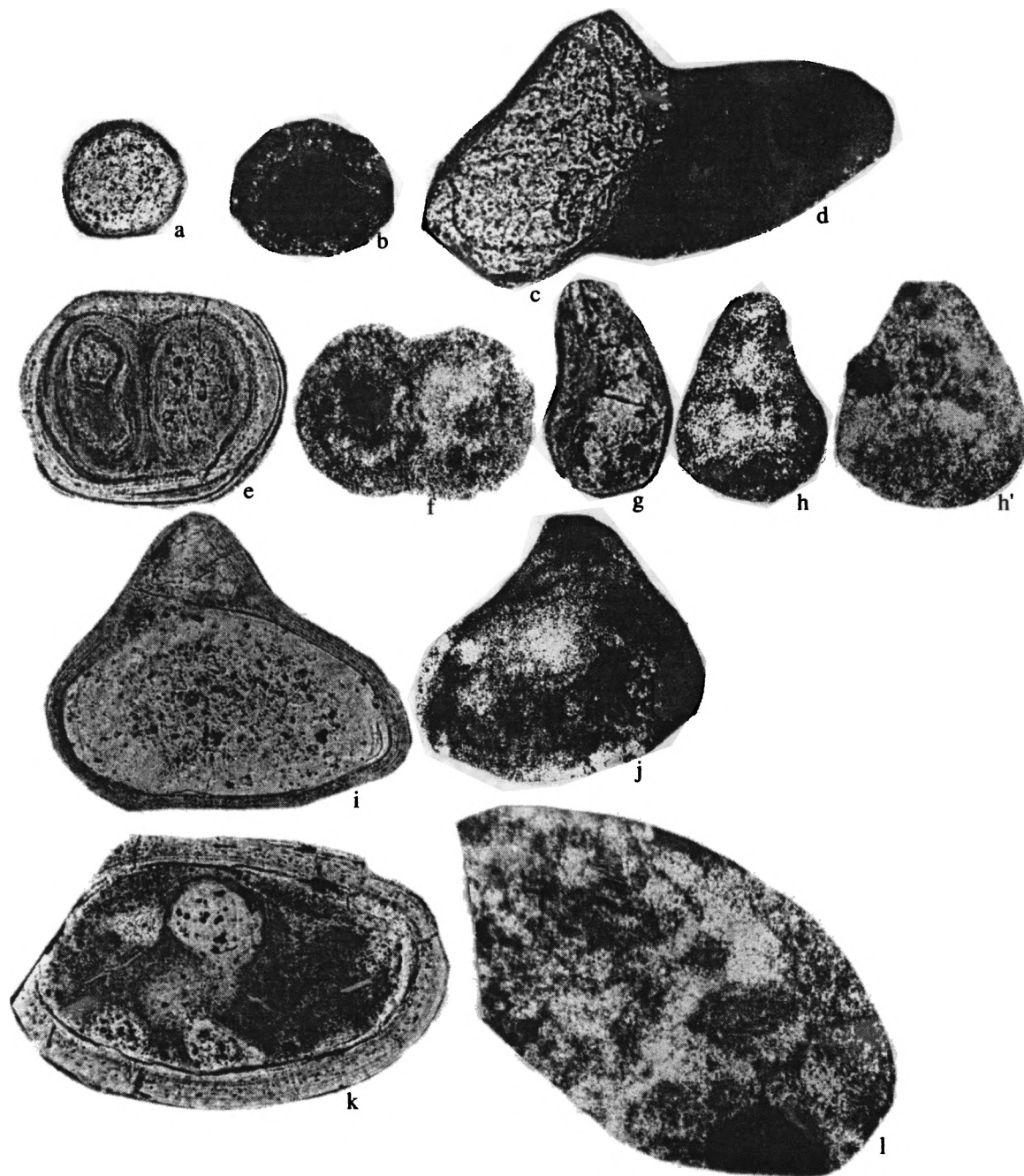


Fig. 4. Comparison of morphologically similar phosphate (a, c, e, g, i, k) and carbonate (b, d, f, h, h', j, l) pellets from the Chulaktau Formation of Karatau. (a, b) Round pellets with a thin fringe: (a) Koksut deposit, Sample 656, magn. 100, (b) Babaata ore occurrence, Sample 988, magn. 100; (c, d) oval pellets joining each other, Zhanatas deposit, Sample 44-D, magn. 250; (e, f) dumbbell-like pellets: (e) Koksut deposit, Sample 630, magn. 250, (f) Babaata ore occurrence, Sample 988, magn. 250; (g, h, h') drop-shaped pellets: (g) Koksut deposit, Sample 988, magn. 200, (h, h') Babaata ore occurrence, Sample 988, magn. 200; (i, j) pear-shaped pellets with laminated fringe: (i) Berkuty Severnyi ore occurrence, Sample 1017, magn. 250, (j) Zhanatas deposit, Sample 44-D, magn. 250; (k, l) large oval oncolite-like pellets with the complex internal structure and several inclusions of simple and small pellets: (k) Babaata ore occurrence, Sample 975, magn. 300, (l) Babaata ore occurrence, Sample 988, magn. 250.

When these results of microscopic mineralogical observations are compared with macroscopic features of silicification and phosphatization of the Chulaktau Formation, on the whole (Kholodov, 1997), it seems

that, following Emigh (1958), one can suggest that carbonate pellets and oncolites represented initial structures in the Tommotian sea. Their intravital and post-mortem phosphatization, first in waters of the sea basin,

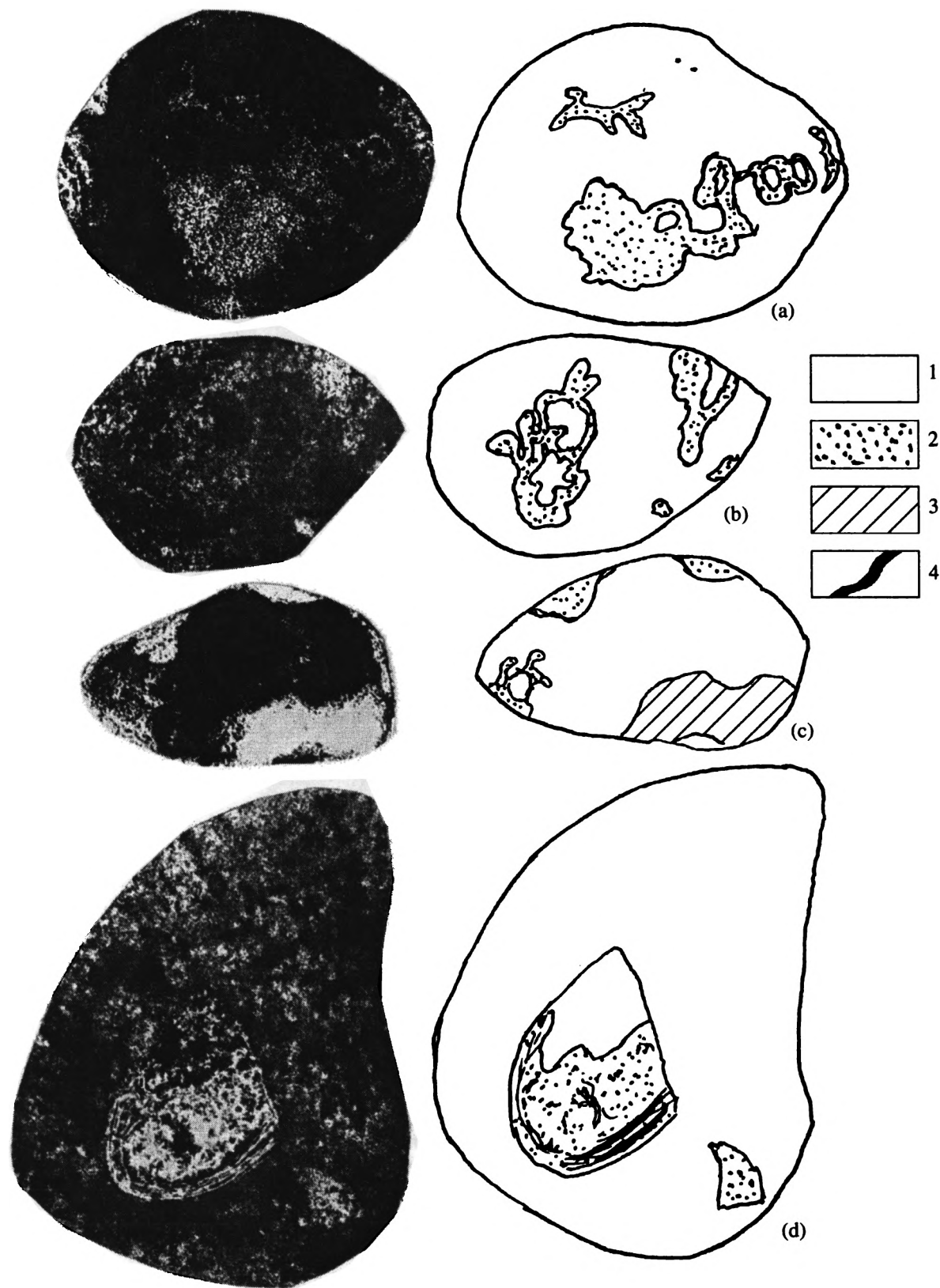


Fig. 5. Morphology and composition of carbonate pellets. (a, b) Zhanatas deposit, Sample 44-D, magn. 100, parallel nicols; (c) Babaata ore occurrence, Sample 988, magn. 100, parallel nicols; (d) Kyrchabakty ore occurrence, Sample 5282, magn. 100, parallel nicols. (1) Dolomite; (2) phosphate; (3) chert; (4) dispersed organic matter.

then in its bottom mud, resulted in the formation of phosphate particles, whereas repeated redeposition and renewal of phosphatization provided a concentration of phosphate pellets composing productive beds.

FACIES OF THE TOMMOTIAN BASIN AND FORMATION MECHANISM OF PHOSPHATE, SILICEOUS, AND CALCAREOUS ROCKS

Three main features of the Tommotian basin controlled phosphorite-forming processes in Lesser Karatau.

(1) A hot arid climate (Strakhov, 1960; Kholodov, 1970a; and others) stimulated the saturation of coastal waters with manganese carbonates; the latter, occurring in seawater in the form of suspension and solution, to a large extent favored the development of bacterial–algal structures. In addition, the flattened topography typical of carbonate platforms (Kholodov, 1997), and the hot arid climate favored formation of shallow-water lagoons with elevated salinity, which, in turn, promoted the development of bacterial–algal microcolonies.

(2) Tectonic processes, and particularly syndimentary faults, were responsible for a system of uplifts and depressions that appeared in the Lesser Karatau region during the Vendian–Tommotian time and represented sedimentary traps in the coastal zone (Kholodov and Koryakin, 1968). A vast shallow-water realm adjacent to the Kokdzhot uplift was divided by a system of shoals, bay barriers, and bridges into shallow basins, whose elongated configuration was approximately parallel with the northwestern, sublatitudinal, and submeridional faults. Abundant underwater barriers separated the areas of phosphorite formation from the open sea and governed relatively quiet hydrodynamics; only sometimes, storms and waves disturbed the accumulated sediments and stimulated edaphogenic processes.

(3) Stable planktonogenic (radiolarian) sedimentation in deeper parts of Greater Karatau resulted in the formation of siliceous–carbonaceous and clayey–carbonaceous sediments with seasonal bedding. Diagenetic sulfate reduction triggered the sulfide formation in bottom mud and H₂S contamination in bottom waters (Ankinovich and Ankinovich, 1966, 1968; Kholodov, 1968, 1973). Similarly to modern sea basins with H₂S contamination (Black Sea, Cariaco Basin, Gotland Deep of the Baltic Sea, Norwegian fiords, and others), waters in the anoxic zone of the Tommotian sea concentrated dissolved SiO₂, P, Mn, and Fe (Kholodov and Paul, 1995; Kholodov, 1997).

Several stages can be distinguished in the formation of phosphorite deposits of Lesser Karatau, which significantly differed in relationships between different facial zones of Lesser and Greater Karatau.

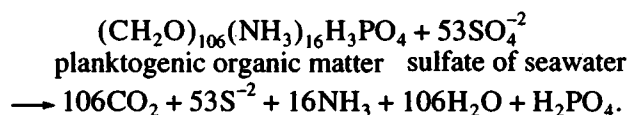
During the *first* stage, Lesser and Greater Karatau were relatively isolated from each other. In Lesser Karatau, shallow-water, well-aerated and heated by

solar energy basins with waters rich in manganese carbonates (suspension + solution), favored a wide distribution of bacterial–algal mats; precisely these structures formed undulate–laminated carbonate sediments, often composing a member of “lower” (Berkuty) dolomites.

Simultaneously, the two processes competed in the coastal zone—bacterial–algal carbonate accumulation and deposition of the pelitomorphic carbonate–clayey material that diluted mats. They alternated and created a peculiar undulate lamination of the dolomitic member. During underwater tectonic (seismic) percussions, laminae easily slipped off each other and, thus, formed bamboo-leaved breccias and peculiar slumping folds.

The northwestern Karatau and Dzhebagly Mountains comprised two depressions partly separated from the previous facial zone by the subaerial Kokdzhot uplift and its underwater continuation. These depressions accumulated thin-bedded carbonaceous–siliceous–clayey sediments, which were mainly formed at the expense of phyto- and zooplankton metabolism; most abundant amid the latter were radiolarians.

Microbiological decomposition of organic-rich mud, in which the sulphate reduction was a leading agent, proceeded according to the following scheme:



The process resulted in the formation of a large amount of H₂S and CO₂, which saturated interstitial waters, formed abundant sulfides by exhausting reserves of Fe and other metals, entered interstitial waters of depressions beyond the system. There, H₂S contamination developed below the wave and current base.

B.A. Tyurin, N.M. Salov, S.G. Ankinovich, and E.A. Ankinovich described many facts confirming anoxic patterns of paleobasins. The general conclusion shared by many researchers was as follows: “...the separation of basins in the Ulutau–Karatau–Naryn and Betpakdala–Zailiskaya zones was followed by the bloom of planktonic organisms, whose dying resulted in the formation of a peculiar H₂S-contaminated environment” (E. Ankinovich and S. Ankinovich, 1966, p. 42).

In addition, interstitial and bottom waters of the Balasauksandyk and Dzhebagly areas were substantially enriched in dissolved P, SiO₂, Fe, and Mn. This is evident from the mean composition of the Kurumsak shales, the occurrence of phosphorite concretions, and also from the wide distribution of authigenic SiO₂, P, Mn, and Fe accumulations.

According to (S. Ankinovich and E. Ankinovich, 1968), primary ores of Greater Karatau are characterized by the following contents of these components:

	Clarke in sedimentary rocks (%)	Average content in ores (%)	Clarke concentration
SiO ₂	50.37	73.72	1.46
P ₂ O ₅	0.16	0.71	4.43
MnO	0.12	0.30	2.5
Fe ₂ O ₃	5.03	5.27	1.04

It is quite evident that sedimentary excess of these chemical elements should be reflected in the composition of H₂S-rich waters of the Tommotian sea. This conclusion is unequivocally supported by the behavior of SiO₂, P, and Mn in Black Sea waters (Kholodov and Paul, 1995).

Principal changes in the facial–paleogeographic setting occurred during the beginning of the deposition of the Chulaktau Formation in Lesser Karatau. As a result of subsidence, this part of the basin fell under the influence of anoxic waters of the Greater Karatau basin strongly undersaturated in carbonates.

Undersaturation of H₂S-rich seawaters with carbonates was closely related to an excess of diagenetic CO₂ that results from the oxidation of organic matter in mud. For instance, the CO₂ content in the anoxic zone of the Black Sea exceeds the average ΣCO₂ content in the Atlantic Ocean (2.2×10^{-3} mol/l according to Wattenberg, 1933) by a factor of 1.3 to 1.9 (Skopintsev, 1979). The latter author emphasized that deep waters of the Black Sea can dissolve both biogenic and terrigenous carbonates. The anoxic H₂S-rich waters could influence sedimentation in Lesser Karatau and, thus, distribution of the carbonate material.

Since the Chulaktau time, bacterial–algal colonies, which earlier intensely consumed carbonates, evolved under a deficiency of carbonates. These carbonates are needed for their vital activity and formation of stromatolite buildups. Biota responded to this new geochemical challenge by a natural change in the most widespread morphologic forms of colonies: stratiform buildups of bacterial–algal mats were replaced by rounded, spherical forms of colonies (pellets). It can be assumed that the advantage of rounded forms, as compared with stratiform structures, was in their larger surface area: the sphere surface is four times as large as the area of its largest cross section, and this feature provides a significantly more intense exchange with the environs and, thus, compensates for the deficiency of required components.

Inasmuch as the close relationships between paleobasins of Greater and Lesser Karatau were retained until the end of the Chulaktau time, the entire Chulaktau succession is mainly characterized by rounded forms of bacterial–algal microcolonies, although locally, stromatolite buildups also occur. The subse-

quent resumption of the carbonate-forming process in the post-Tommotian (Cambrian–Ordovician) time resulted in the reappearance of stratiform and spherical bacterial–algal colonies, as described in Cook *et al.*, (1989), Bazykin (1997), and others.

The *second* stage embraces the lower part of the Lesser Karatau Chulaktau Formation, i.e., the section from the lower siliceous member to the top of the lower phosphate bed.

In Lesser Karatau, this time was marked by the development of a system of synsedimentary faults and biogenic–chemogenic sedimentation, which resulted in the formation of shallow elongated basins (traps) along valleys of the modern Bol'shoi and Maliy Karoi rivers, the Aksai–Aladzhar depression, and along the continuation of these structures. Two different facial settings coexisted and interacted in these basins.

Elevated shoals represented areas with abundant carbonate pelletal bacterial–algal colonies composing sand-to-gravel-sized aggregates that were formed in well-aerated environments under a deficiency of the carbonate material (suspension + solution). In the near-shore zone, this process was complicated by the development of carbonate bacterial–algal mats and small carbonate stromatolite buildups.

Inasmuch as the second stage was characterized by the greater subsidence of Lesser Karatau, as compared with that of Greater Karatau, the deepest parts of basins (traps) were intermittently flooded by denser seawaters with H₂S, and elevated SiO₂, P, and Mn contents, which migrated from the northwest and southeast. These elements could not exist in such environments of "oxidizing basins" for long: H₂S was oxidized to form SO₄²⁻, CO₂ quickly diffused into the atmosphere, whereas SiO₂, P, and Mn precipitated, thus, partly replacing the carbonate bacterial–algal accumulation in sediments and, partly, forming separate laminae.

Atmospheric oxygen dissolved in seawater above shoals and iron hydroxides suspended in coastal waters played a main role in H₂S oxidation: some H₂S was probably decomposed owing to the microbiological processes, as is observed now at the redox boundary in the modern Black Sea (Sorokin, 1982).

The replacement of carbonate bacterial–algal colonies (pellets) by P and SiO₂ was also stimulated by large dimensions of their surface and CO₂ excess in H₂S-rich waters. The limited size of coastal depressions favored the localization of chemical and biochemical reactions, and hindered transportation and dispersion of the precipitating material.

It is also of interest that under conditions of excessive SiO₂ precipitation, some basins (traps) were marked by the accumulation of abundant siliceous microfossils, and by the formation of reefal sponge buildups. The latter probably represented unfirm structures and suffered quick destruction, which is evident from the abundance of siliceous spicules forming inter-

layers and lenses at the base of the phosphorite formation (Kholodov, 1970a).

In general, the second stage was marked by two conflicting, geochemically different facial settings that were developed under conditions of complex and partly flattened topography of sea shoals. The formation of phosphate pelletal sediments commenced with the intravital P_2O_5 accumulation, continued as a postmortem dissolution of carbonate pellets with the replacement of the latter by P and SiO_2 , and terminated by diagenetic metasomatism in semiliquid mud. The metasomatism during erosion eventually formed phosphate-pelletal laminae, lenses, and beds. In the following section of the article, the P_2O_5 behavior at the stage of diagenesis will be discussed in more detail.

The *third* stage of formation of phosphorite-bearing deposits corresponds to the epoch of accumulation of laminated siliceous-clayey-carbonaceous phthanites and shales. Further subsidence in the Lesser Karatau area occurred at that time, and strengthening paleogeographic connections with basins of the Greater Karatau resulted in the accumulation of pure planktonogenic mud with seasonal bedding in the deepest parts of shallow-water basins almost identical to the Kurumsak deep-water facies (Kholodov, 1973). A high concentration of planktonogenic organic matter in the phthanite-facies mud favored intensification of the microbiological sulfate reduction process, formation of the H_2S and CO_2 excess in diagenetically altered mud, their diffusion into bottom waters, and the formation of autochthonous H_2S contamination of the latter. During the third stage, H_2S -rich waters in depressions of the phosphorite-bearing basin represented a product of diagenetic transformation of phthanite facies proper, whereas during the second stage they were allochthonous.

Correspondingly, the role of diagenetic phosphatization and silicification increases. The matter is that the high H_2S and CO_2 contents in interstitial waters of phthanite facies stimulated concentration of dissolved SiO_2 , P_2O_5 , and MnO in the latter. On the other hand, the compaction of phthanite-clayey sediments and pelletal calcareous-phosphate-siliceous mud occurred in different ways. The porosity of pelletal beds and lenses lying under, within, or over the phthanite-clayey mud was only slightly reduced. They corresponded to coarse-grained sands in permeability. Therefore, interstitial waters squeezed out from phthanite-clayey sediments at the boundary of pelletal facies lost H_2S and CO_2 . Consequently, carbonate mats and pellets, that were not subjected to metasomatism in waters of the paleobasin, were diagenetically replaced by precipitating phosphate and SiO_2 . Moreover, the formation of some authigenic phosphate particles, such as spherulites and oolites, occurred precisely in mud. Finally, the subsequent erosion and destruction of phosphate rocks, particularly in contrast redox settings, could promote the further formation of complex phosphate allochems

and terminate the formation of phosphorite stratiform-lenticular accumulations.

Thus, the replacement of carbonate bacterial-algal colonies by P (and SiO_2) generally looks like a multi-stage process that commences during their lifetime, continues in paleobasin waters simultaneously with pellet burial, and terminates at the diagenetic and erosion stage.

The *fourth* stage corresponds to the upper siliceous member and upper phosphorite horizon. The stage was characterized by a general regressive trend. Autochthonous H_2S geochemical facies gradually disappeared from the phosphorite-bearing basin, and vast areas of the considered region came under influence of conflicting allochthonous H_2S -contaminated waters enriched in P, SiO_2 , Mn, Fe, and oxygenated waters with suspended and dissolved carbonate material. Oscillatory migrations of both hydrochemical facies are reflected in the alternation of lithologically different sediments, whereas contrast patterns of these facies created abundant geochemical barriers, which were marked by precipitation or the geochemical reworking of mineralogically variable components. In general, areas with oxygenated waters are marked by a wide development of carbonate bacterial-algal pellets and oncolites, whereas P and SiO_2 were precipitated and accumulated in areas of temporal preponderance of H_2S -rich hydrogeochemical facies.

These geochemical processes reflecting epirogenic oscillations of the paleobasin bottom served as a background against which the directional shoaling of basins (sedimentary traps) and gradual relief peneplanation typical of the period of carbonate platform formation (Kholodov, 1997) took place. This was accompanied by an increase in seawater salinity and the progressive development of lagoonal sedimentation.

Saline lagoonal waters were extremely favorable for the formation of large carbonate bacterial-algal colonies represented by multilayer pellets and oncolites (V.M. Gorlenko, oral communication), whereas water evaporation in a hot arid climate strengthened the precipitation of P_2O_5 , MnO, and SiO_2 from H_2S -rich waters entering from other areas.

As a result of superimposition of many factors during this stage of the phosphorite-bearing paleobasin development, carbonate pellets and oncolites were completely replaced at the earliest phases of the sedimentation process, and phosphorites were characterized by a high P_2O_5 content.

The terminal phase of the fourth stage was marked by the formation of shallow semiisolated pool-like basins filled by bacterial-algal mats and large carbonate-phosphate oncolites with remnants of Fe, Mn, P, and SiO_2 concentrations, representing the last traces of a regressive sea basin in Lesser Karatau. They are described as a "ferromanganese horizon," although carbonate allochems are apparently preponderant in these

facies, whereas the P, Fe, and Mn contents are generally low.

The fifth stage was distinguished by stable oxidizing environments and carbonate accumulation. The biogenic process represented a leading factor, and the cyclicity of events characteristic of carbonate platforms resulted in the formation of thick Cambrian–Ordovician successions. The biological–stratigraphical zonality of phosphorite-bearing deposits of Lesser Karatau, elaborated by Missarzhevskii and Mambetov (1981), is completely in accordance with our lithological–facial stages and even confirms them.

The first level of biota distribution coincides with the first stage of the phosphorite-bearing basin development, and is located in the upper part of the Berkuty dolomite member. The most common conodont form is *Protohertzina anabarica*. The assemblage also includes conodont species *Protohertzina unguiformis*, filamentous algae, stromatolites, and phytolites.

The second biotic level is located at the base of the Chuluktau phosphorite-bearing sequence; in fact, it corresponds with the very beginning of the second lithological–facial stage of the phosphorite-bearing basin development. The most abundant form is hyolithelminth *Pseudortholitheca cutata*. It is accompanied by hyolithelminths *Hyolithellus* and *Torellella*, conodont-like sclerites *Protohertzina siciformis*, *P. anabarica*, anabaritids *Anabarites signatus*, *Tiksitheca*, sponge spicules, *Chancelloria*, hyolithid shells, gastropod remains, and rare poorly preserved phosphate brachiopod shells.

Upward the section, there is a large gap in biota distribution; the latter corresponds to the stage of preponderant H_2S -contaminated facies in sedimentary basins of the considered region.

The third level of wide distribution of fossils is outlined only at the end of the fourth stage; it is confined to the ferromanganese horizon. Most abundant is the tomotioid form *Bercutia cristata* accompanied by hyolithids *Uniformitheca*, *Conotheca mammlata*, tomotioids *Camenella* Miss., *Bercutia* gen. nov., *Geresia* gen. nov., Halkieridae, and others.

The last, fourth level coincides with the base of the Cambrian–Ordovician Tamda carbonate formation, marking a transition to the zonation based on trilobites (Ergaliev and Pokrovskaya, 1977). The most abundant form is represented by conodont *Rhombocorniculum cancellatum*. The assemblage also includes trilobites *Hebediscus orientalis*, *Callodiscus korolevi* Pokr., *Ushbaspis granulata* Pokr., and others like sclerites *Lenastella*, *Cambroclavus*, halkieriids, *Chancelloria*, *Multi-fridea*, *Yochelcionella*, conodont-like *Amfigeisina*, *Hertzina*, *Glauderia*, problematics *Microdyction*, *Monogolotubulus*, *Mobergella*, tomotioids *Ninella serebrjanikovae* sp. nov., Kelanellidae, brachiopods, monoplacophorids, bivalves, gastropods *Palagiella lorenzi* and *Beshtashella tortilis*, stenothecoids, and hyolithids.

It is of interest that all the depicted levels of the biota development are distinctly controlled by oxidizing facies of the Tommotian sea. Fucoids described by Eganov and Sovetov (1979) also associate with interbeds of siliceous–clayey shale formed in oxygenated environments.

The scheme of the Karatau phosphorite-bearing basin evolution discussed here is by no means a final model of pelletal phosphogenesis. It reflects only main features of the regional structure and undoubtedly requires further development and perfection. Nonetheless, in our opinion, it explains significantly more reliably the biogeochemical, petrographic, and lithofacial peculiarities of the Karatau phosphorite-bearing basin and adjacent regions, as compared with the oceanographic hypothesis proposed by A. V. Kazakov or volcanogenic sedimentary hypothesis suggested by N. S. Schatsky.

CONCLUSION

(1) The Lesser Karatau phosphorite horizon retains a diversity of phosphate pellets along the entire profile from deepest to shallow-water facies; simultaneously, large phosphate–carbonate oncolites and fragments of phosphate bacterial–algal mats appear, and the role of phosphate intraclasts increases.

(2) There is a close genetic relation between phosphate–siliceous microfossils, pellets, and oncolites; combined with electron microscope data, it allows all these forms to be considered as typical bacterial–algal microcolonies.

(3) A wide distribution of carbonate oncolites and pellets, their morphological similarity with phosphate structures, as well as the peculiar fact of the partial replacement of carbonate pellets by phosphate and silica, suggest that pellets and oncolites had a carbonate composition.

(4) The change of preponderant forms of bacterial–algal carbonate accumulations from an undulate-laminated structure in the Berkuty time to the rounded, pelletal–oncolitic variety in the Chuluktau time was probably related to the influence of CO_2 - and H_2S -rich waters entering the basin from outside, or forming in its muddy sediments; they aggravated ecological environs and forced microbiological communities to elaborate optimal forms of colonies.

(5) The replacement of carbonate allochems by P and, less commonly, by SiO_2 , Fe, and Mn is explained by the fact that H_2S - and CO_2 -rich waters first concentrated these elements and then released them during oxidation of H_2S in lagoon-like basins (traps). The formation of phosphate pellets seems to represent a complex multistage process, which commenced during the life of bacterial–algal colonies, continued in the water medium of the paleobasin simultaneously with the pellet burial, and then terminated at the stage of sediment diagenesis and even during their subsequent reworking.

(6) Five stages can be distinguished in the evolution of Lesser Karatau phosphorite-bearing formations, all of which were marked by significant changes in the relationships between paleobasins, facies, bottom topography, gas composition, and salinity of waters. Detailed characteristics of the stages are discussed in this work.

(7) The distribution of biotic communities and the stratigraphic position of different biotic levels studied by Missarzhevskii and Mambetov (1981) completely coincide with recognized stages in the development of the phosphorite-bearing basin.

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Metakomatiites in the Ferruginous–Siliceous Formation Section, Kostomuksha Greenstone Belt

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Abstract—Ultramafic schists of the Gimol Group in the Late Archean Kostomuksha greenstone belt (western Karelia) intercalate with ferruginous quartzites, carbonaceous schists, and metagraywackes. Lithological and geochemical data indicate that a portion of the ultramafic rocks are metavolcanics represented by metamorphosed peridotitic komatiite, similar to that from the underlying Ruvivaara Formation of the Kontok Group. Thus, the ultramafic magmatism, products of which are extensively developed in the upper part of the Kontok Group, was extended over the time when the terrigenous (ferruginous–siliceous) formation of the Gimol Group was deposited. Another part of ultramafic schists is represented by basaltic (pyroxenitic) komatiite, which most likely forms relatively young intrusions (sills). The spatial relationships between komatiites and ferruginous quartzites, the geochemistry of quartzites (positive Eu anomaly), and the survey of literature led to the suggestion on the hydrothermal source of Fe and on the relation of hydrothermal activity to the ultramafic magmatism.

Komatiite is an important constituent of the volcanic series in Archean greenstone belts. The chemical and isotopic compositions of these rocks bear information on their origin and serve as sensitive indicators of the geodynamic environment where they were formed.

In the Kostomuksha greenstone belt of western Karelia, metamorphosed ultramafic rocks are known from the volcanogenic Kontok Group and the sedimentary Gimol Group of Late Archean age (Chernov, 1964; Chernov *et al.*, 1970; Gor'kovets *et al.*, 1981) (Fig. 1).

In the Kontok Group, ultramafic rocks are mainly confined to the upper part of the section (Ruvivaara Formation) and occur within a pile of tholeiitic basalts. They often retain a relic spinifex texture, which indicates their volcanogenic origin. The stratigraphic position, composition, and formation conditions of komatiites from the Kontok Group were comprehensively discussed in the literature (Gor'kovets and Raevskaya, 1988; Vrevsky *et al.*, 1996; Puchtel *et al.*, 1997).

In the Gimol Group, ultramafic rocks occur in the lower part of the section (Kostomuksha Formation), where they intercalate with ferruginous quartzites, carbonaceous schists, and metagraywackes. Chernov considered these rocks to be metamorphosed lavas and tuffs (Chernov, 1964; Chernov *et al.*, 1970). Subsequently, they were regarded as intrusive rocks and excluded from the section (Gor'kovets *et al.*, 1981; Gor'kovets and Raevskaya, 1988). The stratigraphic position and petrography of ultramafic rocks were described in detail in the above works; however, the geochemistry did not attract the attention required. At the same time, the composition of ultramafic rocks and their origin have principal implications for the geody-

namic environment where the ferruginous–siliceous–terrigenous Gimol Group was deposited (Gor'kovets *et al.*, 1981). In particular, it is important to answer the question of whether the Gimol Group is a direct continuation of the Kontok Group section, as was assumed by Gor'kovets *et al.* (1981) or whether it makes up an autonomous sedimentary terrane, as suggested by Puchtel *et al.* (1996, 1997). The origin of ultramafic schists intercalated with ferruginous quartzites may also provide insights into the source of Fe. The lithology and geochemistry of metamorphosed ultramafic rocks in specific sections of the Gimol Group, which are reported in this paper, allow an approach to the solution of these problems.

GEOLOGICAL SETTING AND PRIMARY NATURE OF ULTRAMAFIC ROCKS

Ultramafic rocks were studied in cores from two boreholes (Figs. 1, 2). Five ultramafic interlayers, 1–10 m thick, were recognized in the borehole 1568 section having a total thickness of 570 m. Three interlayers are clearly related to lower contacts of magnetite quartzite and upper contacts of metaterigenous rocks represented by metagraywacke or carbonaceous schist. One interlayer, 1 m thick, occurs within carbonaceous schists, and another, 10 m thick, is sandwiched between the carbonaceous schist and ferruginous quartzite. The rocks underwent epidote–amphibolite-facies metamorphism.

Presently, ultramafic rocks are devoid of primary texture and represented by talc–chlorite, tremolite–chlorite, and chlorite–actinolite rocks with a variable

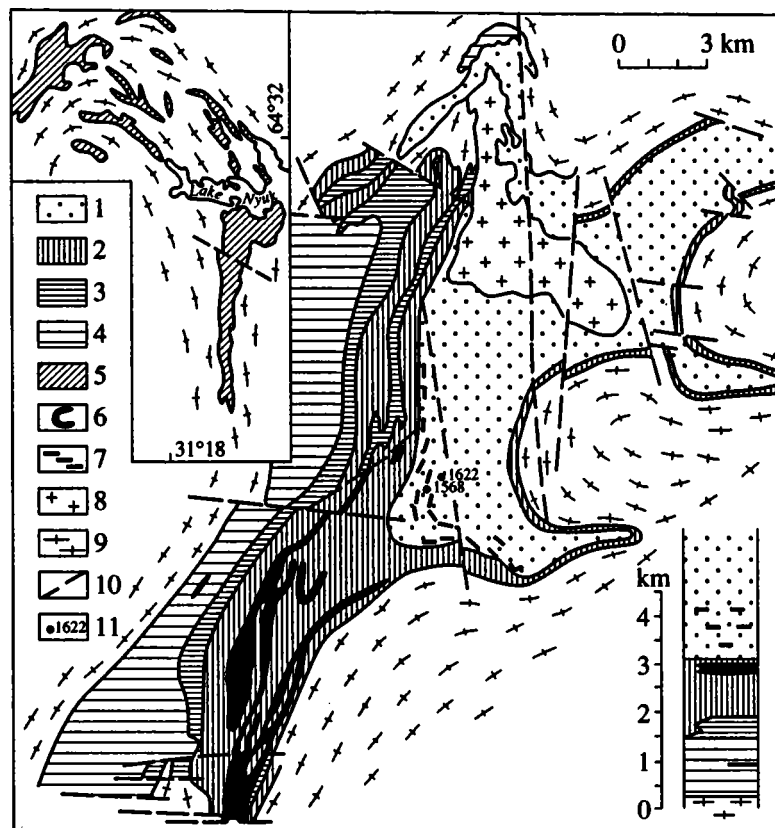


Fig. 1. Schematic geological map of the Kostomuksha greenstone belt, after Gor'kovets and Raevskaya (1988). (1) Metasedimentary rocks of the Gimol Group; Kontok Group; (2) basic volcanics (Ruvinka Formation), (3) acid volcanics (Shurlovaara Formation), (4) basic volcanics (Niemijarvi Formation); (5) supracrustal rocks in greenstone belts of western Karelia (unspecified); (6) metakomatiite of the Kontok Group; (7) metakomatiite of the Gimol Group (symbols are out of scale); (8) two-feldspar and microcline granites; (9) granitic gneiss; (10) faults; (11) location of borehole and its number.

amount of dolomite and magnesian biotite. As a result, the metamorphic schists are enriched in CaO , CO_2 , K_2O , Rb, and Sr, i.e., in elements, which are not typical of ultramafic rocks (Table 1). The least altered samples, 1568/71 and 89, are close in composition to peridotitic komatiite. The upper (1–3 m) layers under consideration are dolomitized rocks with porphyroblasts and lenses of Mg-rich biotite rather than true ultramafics. Biotite-carbonate rocks are characterized by a rough lenticular banded structure and low or even negligible Cr, Ni, Co, and V contents in comparison with ultramafic rocks; they are also depleted in MgO and enriched in K_2O at the expense of mica (Table 1, samples 1568/77, 1568/103). The specific type of rock succession (ultramafic schists overlapped by biotite-carbonate rocks) was previously reported by Chernov (1964).

Such relations allow us to suggest that we are dealing with thin komatiite flows, which have undergone severe diagenetic alteration. The dolomite was likely formed as a carbonate suspension. The decomposed komatiite served as a local source of Mg, while the seawater was a source of CO_2 and CaO . The micaceous mineral was precipitated as a K-rich Fe-Mg-smectite, which subsequently metamorphosed into biotite.

According to Strakhov (1956) and Bezborodova (1987), the diagenetic dolomite deposition is possible at a slow sedimentation rate, when the rocks are located in contact with seawater and are not overlapped by sediments for a long time. Similar conditions were favorable for the smectite formation. As is indicated by apparently clastic plagioclase and quartz grains in upper parts of biotite-carbonate interlayers, the diagenetic alteration was interrupted by a supply of terrigenous material. These rocks are enriched in Na_2O relative to the underlying komatiite (Table 1).

Secondary dolomite, occasionally together with phlogopite or magnesian biotite, is abundant in Late Archean metakomatiites and commonly refers to metasomatic or hydrothermal processes superimposed on ultramafic rocks (Tourpin *et al.*, 1991 and others). Although the mineral composition of altered komatiite is similar to the rocks under discussion, the specific position of biotite-carbonate rocks in the section more likely indicate their diagenetic origin and allow us to regard the related ultramafic rocks as supracrustal.

The upper supraore part of the Gimol Group section (borehole 1622) comprises two conformable interlay-

ers of ultramafic rocks which are not confined to a specific lithology, as in the lower part (borehole 1568). The lower interlayer, 50 m thick, is hosted by a meta-graywacke, whereas the upper interlayer, 10 m thick, occurs between the underlying graywacke and overlying ferruginous quartzite. Ultramafic rocks are represented by a talc-chlorite-tremolite schist with an insignificant admixture of carbonate and biotite. Biotite-dolomite units were not observed.

ROCK CHEMISTRY

Ultramafic schists from lower and upper parts of the section (boreholes 1568 and 1622, respectively) differ not only by their geological setting and secondary alteration, but also by composition. Ultramafic rocks from borehole 1568 are represented by komatiite with 30–34 wt % MgO (recalculated to 100% volatile-free). Based on the FeO/MgO ratio and the assumption of a positive correlation between the Fe/Mg ratio and the liquidus temperature of magma (Roeder and Emslie, 1970), the liquidus temperature of komatiite calculated from (Nisbet *et al.*, 1993) turns out to be 1600–1650°C. In major and trace element compositions, the rocks under consideration are close to Ruvinvaara Formation komatiite, Kontok Group (Table 1). They are characterized by a flat REE pattern with the bulk REE contents of 3–6 times higher than those in chondrites where La/Sm and La/Yb ratios close to unity (Table 2, Fig. 3). The absence of a negative Nd anomaly in the sample 1568/71, as is evident from $(Nd/La)_N > 1$, testifies to the absence of komatiite contamination by crustal material. Ultramafic rocks from the upper part of the section (borehole 1622) are depleted in MgO, enriched in Zr and LREE with $(La/Yb)_N = 4–7$ and have a negative Nd anomaly, as indicated by $(Nd/La)_N = 0.6$ (Table 1; Fig. 3). The distribution of trace elements, including REE, indicates that all these rocks are contaminated komatiites or picrites. Most likely, they are related to young intrusions (sills).

Thus, at least a portion of ultramafic rocks from the Gimol Group is represented by metavolcanics, and more precisely, by peridotitic komatiite, which is geochemically similar to komatiite from the Ruvinvaara Formation. Hence, the extensive ultramafic magmatism of the Kontok Group persisted to develop during the deposition of ferruginous-siliceous rocks of the Gimol Group. Hence, the Gimol Group is a continuation of the Kontok Group, rather than an autonomous terrane representing the ancient continental margin (Puchtel *et al.*, 1996, 1997). The high-temperature ultramafic magmatism of the Kontok Group was related to the mantle plume (Puchtel *et al.*, 1997; Vrevsky *et al.*, 1997), which continued to exist during the deposition of Gimol rocks.

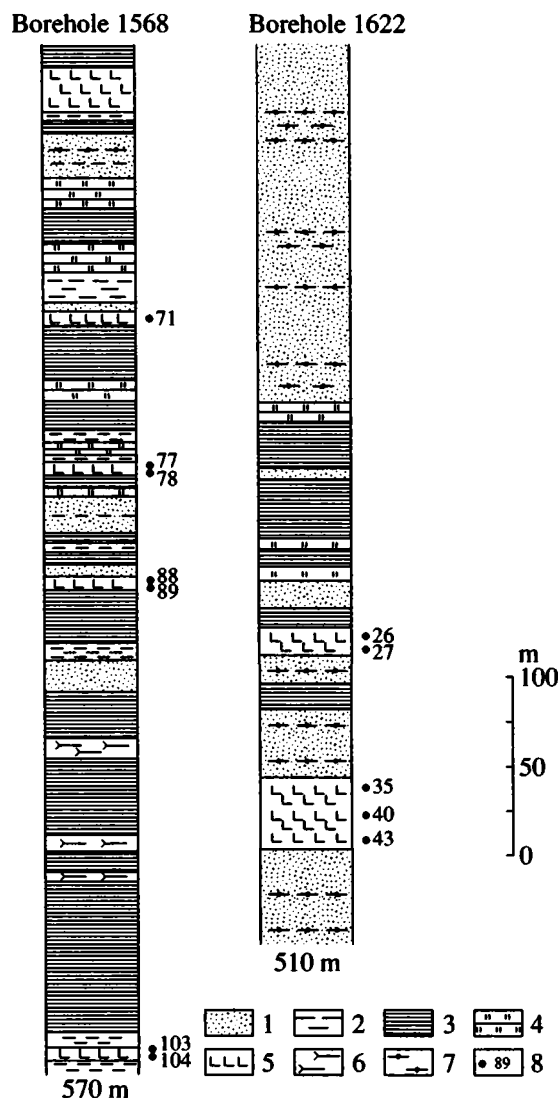


Fig. 2. Borehole sections of the Gimol Group. (1) Biotite-feldspar-quartz schist (metagraywacke); (2) carbonaceous schist; (3) magnetitic quartzite; (4) silicate and biotite-grünerite schists; (5) metakomatiite; (6) subvolcanic dacite; (7) altered rocks; (8) location of a sample and its number. See Fig. 1 for the borehole location.

KOMATIITES AND FERRUGINOUS QUARTZITES

Considering the composition and geological setting of ultramafic rocks of the Gimol Group, we would like to note that they intercalate with ferruginous quartzites, which make up a large iron ore deposit. The areas of ultramafic rocks and ferruginous quartzites coincide. Ferruginous quartzite is characterized by a positive Eu anomaly (Fig. 3). As established for the recent metalliferous sediments in the Red Sea (Butuzova and Lyapunov, 1995) and some Late Archean ferruginous quartzites (Barret *et al.*, 1988; Bau and Dulski, 1996), the positive Eu anomaly indicates a hydrothermal ori-

Table 1. Major oxide (wt %) and trace element (ppm) contents in komatiites from the Kostomuksha greenstone belt

Component	1568/71	1568/77	1568/78	1568/88	1568/89	1568/103	1568/104	1622/26	1622/27	1622/35	1622/40	1622/43	82	109
SiO ₂	41.88	26.67	28.55	31.53	39.89	42.54	31.39	47.56	45.58	48.86	40.90	47.64	43.20	42.48
TiO ₂	0.31	0.19	0.26	0.21	0.24	0.55	0.42	0.48	0.48	0.51	0.35	1.04	0.29	0.41
Al ₂ O ₃	6.20	5.44	5.36	5.97	4.58	10.53	7.40	7.60	7.94	9.48	4.95	16.15	6.10	7.75
Fe ₂ O ₃	2.76	1.14	2.30	1.07	2.59	2.90	2.14	2.63	2.01	2.35	1.46	4.40		3.63
FeO	5.56	5.45	5.34	5.67	6.87	6.76	6.76	5.78	6.21	5.45	6.10	7.63	10.18	7.49
MnO	0.07	0.21	0.27	0.26	0.07	0.14	0.17	0.08	0.11	0.10	0.10	0.10	0.14	0.11
MgO	26.19	18.09	21.84	12.64	27.21	12.00	21.10	24.05	24.46	19.96	27.60	9.01	25.41	25.32
CaO	3.93	15.14	12.50	16.43	4.94	8.28	10.18	4.79	7.14	5.84	7.31	11.94	4.97	5.56
Na ₂ O	0.10	0.07	0.10	0.87	0.07	0.99	0.10	0.30	0.20	2.30	0.20	0.38	0.36	0.21
K ₂ O	3.70	1.57	0.74	1.89	0.08	2.44	1.49	2.63	1.31	0.01	0.12	0.12	0.15	0.04
P ₂ O ₅	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.12	0.10	0.10	0.03	0.02	0.04	0.02
CO ₂	5.90	24.96	20.38	22.10	8.00	11.43	15.62	1.14	0.38	0.20	5.71	0.20		
L.O.I.	8.55	25.50	21.83	22.57	12.95	11.92	18.14	3.46	3.95	3.53	10.34	1.09	8.24	6.57
Total	99.55	99.88	99.88	99.62	99.51	99.7	99.6	99.52	99.51	99.52	99.62	99.50	99.26	99.59
Rb	166	50	27	17	5	111		136	57	36	9	9	4	1
Sr	47	110	163	50	118	150		40	22	143	546	125	11	12
Y	7	5	6	5	6	14		11	13	14	11	12	8	8
Zr	35	18	23	15	24	35		63	64	74	30	63	20	22
Nb	6	<1	5	5	5	5		6	6	5	4	7	1	1
Ba	132	26	100	133	100	246		376	477	219	100	121	54	78
Cr	1549	1790	2019	10	2370	724		1843	1715	1435	2409	1828	3184	2979
Ni	1275	930	817	5	1328	185		808	788	637	1096	837	1627	924
Co	69	56	54	27	71	45		50	44	49	61	55	103	103
V	119	99	138	30	136	217		151	132	148	116	140	107	196

Note: Samples 82 and 109 are from the Kontok Group, other samples are from the Gimol Group. Microprobe analyses of carbonate and mica from samples 1568/77 and 1568/103 yielded the following results (formula units). 1568/77 (dolomite): Ca 0.475, Fe 0.76, Mn 0.006, Mg 2.024; 1568/77 (phlogopite): Si 2.85, Ti 0.064, Al 1.346, Fe 0.624, Mn 0.06, Mg 2.024, K 0.833, Cr 0.045; 1568/103 (dolomite): Ca 0.490, Fe 0.100, Mn 0.013, Mg 0.397; 1568/103 (Mg-rich biotite): Si 2.794, Ti 0.083, Al 1.464, Fe 0.916, Mn 0.005, Mg 1.730, K 0.795.

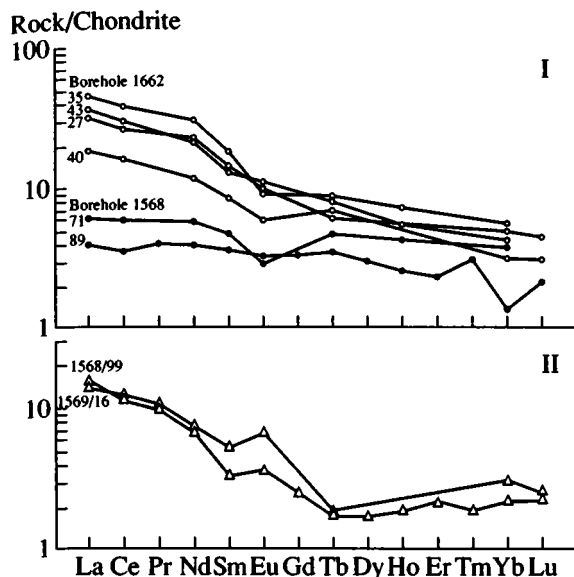


Fig. 3. REE patterns of (I) komatiites and (II) ferruginous quartzites of the Gimol Group. Numerals are sample numbers (see Table 2).

gin of rocks. The hydrothermal source of Fe may also infer to the ferruginous quartzite from Kostomuksha. Taking into account the spatial interrelation of metakomatiites and ferruginous quartzite, the genetic relation of the hydrothermal activity to ultramafic volcanism may be suggested. This suggestion is supported by data on present-day ore-forming systems.

The study of the Red Sea rift and other riftogenic zones in the World Ocean yielded following principal results:

(1) Metalliferous and ore-bearing sediments with iron hydroxides and silica (major components) and a

Table 2. REE contents (ppm) in metakomatiites and ferruginous quartzites from the Gimol Group in the Kostomuksha greenstone belt

	1568/89	1568/71	1622/35	1622/43	1622/40	1568/99*	1569/16*
La	1.17	2.2	16	13	7.2	5.9	5.5
Ce	2.97	<6	37	29	18	11	12
Nd	2.19	<4	24	16	8.7	5.5	7.2
Sm	0.675	1.23	4.31	3.32	2.08	0.78	1.13
Eu	0.212	0.2	0.86	1.0	0.54	0.33	0.55
Tb	0.133	0.31	0.52	0.43	0.43	<0.2	<0.2
Ho	0.158	0.39	0.63	0.53			
Yb	0.365	1.0	1.4	1.1	0.78	0.45	0.70

Note: Samples 1568/99 and 1568/16 are ferruginous quartzites; other samples are komatiites.

small amount of smectite are related to hydrothermal activity.

(2) Hydrothermal activity was of pulsatory character; it varied with time and was related to small isolated intracrustal magmatic chambers.

(3) Hydrothermal fields are associated with high-Mg lavas, which were accumulated in small transitional intracrustal magmatic chambers. The filling of magma chambers was accompanied by the release of a great amount of thermal energy, which stimulated the hydrothermal convection (Butuzova, 1991; Butuzova and Lyapunov, 1995).

Ultramafic rocks and ferruginous quartzites form several cycles in the Kostomuksha section (Gimol Group). The composition of rocks, which intercalate with ferruginous quartzites, indicates that the sedimentation basin was not permanently enriched in Fe. The average Fe content in the metagraywacke of the Kostomuksha Formation ($\text{Fe}_3\text{O}_{4\text{total}} = 7.14 \text{ wt } \%$) reported by Mil'kevich and Myskova (1998) is similar to that of typical Late Archean metagraywacke (Taylor and McLennan, 1988). Komatiites and their diagenetic alteration products (biotite-dolomite rocks) contain commensurable amounts of Fe (Table 1). Hence, during diagenesis, the komatiites were the sole source of Fe, and the seawater was not enriched in Fe at that time.

The inferred hydrothermal source of Fe allows us to explain the stratigraphic position of metakomatiite between underlying ferruginous quartzites and overlying terrigenous rocks. Hydrothermal activity resulted in the deposition of ferruginous quartzite. The later komatiite effusion was followed by a hiatus under quiet geodynamic conditions and a severe diagenetic alteration of bedrock. Subsequently, the geodynamic reactivation gave rise to the deposition of terrigenous rocks.

The negative Eu anomaly in some komatiites from the Kostomuksha and Ruvinvaara formations was explained by Vrevsky *et al.* (1997) by a migration of Eu into the postvolcanic hydrothermal fluid of the black-smoker type. These authors referred the ultramafic volcanism to the mantle plume beneath the Kostomuksha greenstone belt. From this standpoint, the formation of the iron ore deposit therein seems to be reasonable. The negative Eu anomaly in komatiite is consistent with a positive Eu anomaly in ferruginous quartzite.

CONCLUSION

Ultramafic rocks are known from the lower part of the Gimol Group (Kostomuksha Formation), where they intercalate with ferruginous quartzites, carbonaceous schists, and metagraywackes. Previously, the ultramafic rocks were often referred to as intrusions and were excluded from the stratigraphic section.

Based on the stratigraphic position, composition, and lithological and geochemical signatures, ultramafic schists are divided into two groups.

The ultramafic schists of group 1 occur within carbonaceous schists or are confined to the contact of ferruginous quartzite (lying wall) and metaterrigenous rocks (hanging wall); the thickness of interlayers varies from 1 to 10 m. They are represented by talc-chlorite, tremolite-chlorite, and chlorite-actinolite rocks devoid of primary textures and contain a variable amount of dolomite and magnesian biotite. The upper layers (1–3 m) are composed of dolomitic rocks with porphyroblasts and lenses of biotite. Such composition and structure of interlayers allowed us to suggest that we dealt with thin komatiite flows, which underwent severe diagenetic alteration. According to Strakhov (1956), this is possible when the sedimentation rate slows down and the bedrock is located in contact with seawater for a long time, while not being overlapped by sediments. The geochemistry of ultramafic schists of group 1 fits the peridotitic komatiite and is similar to that of the komatiite from the Ruvinaara Formation (Kontok Group). They are characterized by a flat REE pattern with a bulk REE content, 3–6 times higher than the chondritic level, and by an absence of negative Nd anomaly, thus indicating that the primary melt was not contaminated by crustal material.

Ultramafic schists of group 2 do not reveal a clear relation to specific sedimentary rocks. Their composition matches the pyroxenitic komatiite (or komatiitic basalt), and most likely they make up relatively young intrusions. These rocks are enriched in Zr and LREE and have a negative Nd anomaly, indicating a possible contamination of the primary melt by a crustal material.

The data obtained lead to the conclusion that ultramafic volcanism, which produced igneous rocks of the underlying Kontok Group, persisted to be active during the deposition of terrigenous ferruginous-siliceous rocks of the Gimol Group. Hence, the Gimol Group is most likely a continuation of the Kontok Group section rather than an autonomous terrane related to the ancient continental margin (Puchtel *et al.*, 1997). The high-temperature ultramafic magmatism of the Kontok Group is related to the mantle plume (Puchtel *et al.*, 1997; Vrevsky *et al.*, 1997), which persisted to exist during the deposition of the Gimol Group rocks.

By taking into account the spatial association of komatiites and ferruginous quartzites, the geochemistry of ferruginous quartzite (positive Eu anomaly) and other data reported in the literature, we infer the hydrothermal source of Fe and the relationship of the hydrothermal activity with ultramafic magmatism.

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Some Types of Nodular Jaspers from Accreted Effusive–Siliceous Oceanic Complexes, Northeast Russia

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Abstract—Upper Paleozoic and Mesozoic effusive–siliceous sequences, exposed within different terranes of the Koryak–Kamchatka Fold Belt (northeast Russia), include nodular jaspers with a specific composition. They fill separate inter-pillow cavities in the upper part of oceanic-type basalt flows or are encountered in the form of crust and lenslike deposits at the boundary of lavas and overlying pelagic radiolarites. In all instances, the nodules, up to several millimeters in size, have a spherulitic texture of different types. From the standpoint of chemical composition, the jaspers are characterized by a high content of SiO_2 (~90%) and Fe, as compared with other major components (Fe_2O_3 3–9%). The very low total REE content (up to 10 ppm) is a characteristic feature. The distribution of these elements, as in the host tholeiite, shows a sharp enrichment in HREE relative to LREE: the PAAS-normalized La_n/Sm_n and La_n/Yb_n values are equal to 0.22–0.28 and 0.06–0.07, respectively. Jaspers have a quartz–lutecite or quartz–chalcedony–lutecite composition. In the last case, chalcedony makes up nodule cores. The crystalloptical models for chalcedony and lutecite are reviewed. The formation of jaspers is related to the precipitation of silica from thermal solutions. The geochemical peculiarities of the jaspers under study are explained by the specific features of these solutions. It is supposed that the formation of the solutions was tied to the metamorphic transformation of seawater captured by lavas and its interaction with basaltic glass. The formation of chalcedony took place in line with the crystallization scheme of gel that precipitated from a colloidal solution under a sharp temperature gradient and, accordingly, a sharp fall in the solubility of silica, including its amorphous forms. Lutecite is supposed to be formed as a result of the instantaneous precipitation of skeletal-type crystals from solutions oversaturated in quartz. The origin of oversaturation was favored by a gradual decrease in temperature. The relics in chalcedony and lutecite sectors of the nodules with thin zonal structures, which are the result of autooscillation, testify to the participation of ferruginous–siliceous gels in the formation of the jaspers.

Upper Paleozoic and Mesozoic effusive–siliceous sequences are locally found within many terranes in northeast Russia. Based on petrogeochemical features of the volcanics and the facial type of sedimentary deposits, the majority of these sequences is considered to be accreted fragments of oceanic plates. Sedimentary components of sequences associated with the effusives are represented by different siliceous, siliceous–clay, and silty–pelitic rocks. The composition of the latter is normally characterized by the presence of volcanimictic material. Biogenic varieties, mainly red radiolarian jaspers and radiolarites, predominate among siliceous rocks. The additional abiogenic siliceous rocks having a macroscopically well-defined nodular texture are subordinate, as compared with the above listed rocks. Nevertheless, they are a characteristic member of the associations under consideration. Therefore, such rocks must also be taken into consideration during the comparison of formational complexes making up the upper crust of the modern oceans and oceanic fragments accreted to the fold belt framing. The study of mineralogical composition of nodular jaspers showed that the nodules, completely or partially, consist of lutecite (fibrous quartz with oblique extinction and positive elongation of fibers).

In relatively few publications dealing with fibrous quartz, special attention is given to quartzine and lutecite. The work by Folk and Pittman (1971) promoted a common notion that length-slow varieties of fibrous quartz precipitate under high pH or in the presence of sulfates. Both minerals were considered to indicate the presence of evaporitic carbonates or sulfates and are cited as evidence for very shallow-water or even terrestrial evaporitic conditions in the past. For instance, the presence of quartzine was assumed as evidence for the shallow-water nature of the novaculite genotype from the Devonian Caballos Formation in Western Texas (McBride and Folk, 1977). The analogous “facial” assessment of quartzine can be found in other papers (Arbey, 1980; Milliken, 1979; Siedlecka, 1972, 1976; West, 1973; etc.).

The presence of rocks containing length-slow varieties of fibrous quartz, in some terranes of the western rim of the Pacific, is known from papers of Japanese geologists (Tsukamoto, 1989; Mizutani *et al.*, 1987). These minerals were discovered in Mesozoic units cropping out to the south and north of the Mino Terrane in Central Japan. In the southern area, quartzine and lutecite are encountered among Middle Triassic jaspers, including sandstone interlayers (Tsukamoto,

1989). Diagenetic (after H. Tsukamoto) lutecite, together with other forms of fibrous quartz, fill tensile (normal to bedding) fractures in white cherts. Separate interlayers of these cherts occur concordantly in red, platy radiolarian jaspers. In fractures, the interrelation of lutecite with other forms of quartz is quite regular: sidewalls of fractures are covered by chalcedony with a thin coating of lutecite and quartzine. The central sector is filled with mosaic quartz. Quartzine, in contrast to lutecite, is also found in other successions of fracture infilling: chalcedony-quartzine-mosaic quartz, quartzine-chalcedony, and mosaic quartz-chalcedony-quartzine-mosaic quartz. In veinlets of the latter type, the central core sometimes includes aggregates of pseudo-cubic fortificational-zonal quartz. The latter was treated by H. Tsukamoto to be a pseudomorph developed after a halite-type mineral.

Electron microscopy showed that white cherts contain numerous pseudolepispheres that are very similar to those observed in the Caballos novaculites. Based on this information, Tsukamoto suggested that white cherts, like novaculites, are silicified limestones. Though the Triassic siliceous Mino Formation differs from the Caballos Formation, the origin of lutecite and quartzine in white cherts was considered by Tsukamoto as in traditional form, in accordance with the idea of Folk and Pittman. At the same time, taking into consideration the results of experiments carried out by Oehler (1976) and the investigations executed by Flörke *et al.* (1976), Tsukamoto came to the conclusion that quartzine may also be formed under other conditions. He noted that only lutecite, only if it does not occur in basalts, can be taken as an indicator of evaporitic conditions (Tsukamoto, 1989).

There are many other facts to testify that quartzine and lutecite, at least in some cases, are not evidence to prove shallow-water evaporitic conditions. For example, based on the study of Maestrichtian and Campanian marine coquina in Syria, Murav'ev (1989) revealed that all varieties of fibrous quartz are present in a single sample, and even within a single field of view in a thin section. He demonstrated that chalcedony is formed from gel, whereas lutecite is precipitated from an oversaturated solution of silica monomers (relative to quartz solubility). He noted that fibrous quartz is developed in various stages in the process of limestone silicification. According to Murav'ev, the formation of fibrous quartz varieties in the Syrian coquina was first of all dictated by the concentration of dissolved silica relative to the solubility of amorphous silica or quartz.

Study of the sequences drilled by the R/V *Glomar Challenger* in the Northern Pacific during Leg 32 showed that deep-water pelagic cherts and porcellanites contain all types of fibrous quartz: different types of chalcedony, quartzine, and lutecite (Keene, 1983). Quartzine was found both in cherts and underlying basalts. In all cases, it occurred in association with

authigenic barite and frequently with authigenic dolomite. According to Keene (1983), quartzine formed at a diagenetic stage during the last phase of silica precipitation between the precipitation of barite and dolomite; the interrelations of granular quartz, quartzine, and banded "zebralike" chalcedony, observed in the association, reflect the diagenetic history of the rock and particularly the changes of interstitial solutions with time. Keene supposed that quartzine precipitated from the saturated (relative to the quartz solubility) solution of silica, when the pore fluids were rich in magnesium and sulfate ions. This conclusion was based on experimental results of Kastner (1980) related to quartzine synthesis.

Lutecite in oceanic sediments studied by Keene (1983) was significantly less common than quartzine and was confined to the contact between pelagic sediments and underlying basalts. The photomicrograph of a thin section presented by Keene (1983) shows that lutecite forms a nodule with a diameter of not less than 3 mm and a characteristic chevronlike interrelation of fiber clusters. It was supposed that lutecite precipitated from a hydrothermal solution related to cooling basalts.

Thus, today there is no doubt that the concept of the role of quartzine and lutecite, as an indicator of shallow-water conditions during the formation of the host deposits, is wrong. As has long been noted by Oehler, there is a need for the development of a more rigorous general theory for the formation of optical varieties of fibrous quartz under the influence of variable conditions. The data presented in this paper are of great interest in this respect because they deal with specific formational complexes, including basaltic flows.

GEOLOGICAL SETTING AND PETROGRAPHIC FEATURES OF NODULAR JASPER

The nodular jaspers discussed below were studied in three separate areas of the Koryak-Kamchatka Fold Belt. Each of these areas occupies a different structural-formational position in the modern structure of the northwestern rim of the Pacific Ocean. During recent years, in tectonic schemes of the Pacific Ring, these zones are more frequently considered as terranes. Additionally, in areas where the nodular jaspers were studied in exposures, fragments of similar jaspers are often encountered in taluses, recent channel alluvium from many rivers of the Koryak Highland, and in adjacent regions of northeast Russia. Moreover, pebbles of analogous jaspers are present among some Upper Cretaceous conglomerates. This permits us to suppose that the nodular jaspers, akin to studied ones, may be found in significantly more numerous locations in effusive-siliceous sequences of the Koryak Highland. In this respect, very interesting data were cited by Khotin (1976) on the Upper Cretaceous effusive-tuffaceous-siliceous formation of Cape Kamchatka. Among rocks making up this formation, he defined and described "spherulitic chalcedonic jasper" as being very similar

to the luteitic type of nodular jaspers in appearance, paragenesis with basalts, general chemical composition, and structure of bundles of fibers forming spherulites. Unfortunately, the crystalloptical varieties of fibrous quartz ("chalcedony"), making up these spherulites, were not examined by Khotin. But on the other hand, he revealed in detail the position of these jaspers in sequences. It is established that, in Cape Kamchatka, similarly to other terranes of the Koryak Highland, "spherulitic jaspers" are minor constituents of the formation. These jaspers form small nodules and lenses close to the top of basaltic flows or on their surface. They also make up the base of separate jasper-carbonate units, in which the thickness of spherulitic jaspers is not more than 5 cm. The analogous pattern of nodular jasper distribution is also seen in other areas described below. We think that this pattern points out definite genetic conditions as being rather accidental.

Area 1 (observation point M-232), where the nodular jaspers were examined, is located in the upper reaches of the right tributaries of the Emravaam River (a divide between the heads of the Khatyrka, Vaegi, and Pikas'vayam rivers). The area is composed of Tithonian-Neocomian effusive-siliceous rocks of the Nizhnii Chirinaï tectonic slab. The latter, in turn, is incorporated in the Emravaam-Pikas'vayam nappe system (Grigor'ev *et al.*, 1986, 1987). In general, this system is reminiscent of Franciscan terranes in the formational composition of relevant complexes, frequent cataclasm of rocks, and alteration degrees corresponding to the high-pressure (up to glaucophane facies) conditions (Sokolov *et al.*, 1997).

The area under consideration exposes a sequence, about 50 m thick, consisting of massive basalt flows, basaltic breccia beds, volcanimictic sandstone lenses, and siliceous rock units with radiolarian remnants. The total thickness of the siliceous units is up to 20 m. A 1- to 2-cm-thick layer, enriched in small basalt clasts and feldspar grains (edaphogenic admixture), is observed in places at bases. The color of the siliceous rock is red in the lower parts of the units, but upward the section it gradually becomes greenish.

A locally developed lens of the nodular jaspers is situated at the base of the siliceous unit. Judging from the observed extent of its exposure (~25 m), the distribution area of these jaspers on the top of basalts can be first estimated to be hundreds of square meters. The maximum thickness of the lens is about 40 cm. The jaspers gradually pinch out towards its margins. The nodular structure is best defined in the thickest place and less pronounced in the pinchout zones. The nodular structure is well seen against the general red background of the rock, due to white or light gray color of the central parts of nodules (cores). Dimensions of nodules vary from 1 to 7 mm. A characteristic feature is the confinement of sectors with larger nodules to the lower parts of the lens, where separate nodules or blobs of several converged nodules are included in the basal red

(ferruginous-siliceous) matrix. The upper part of the lens consists of relatively smaller converged nodules with a filmy matrix. In both cases, the matrix is represented by granular quartz with a large quantity of flaky hematite.

At the base of the nodular jasper, on the surface of the underlying basalt, there is, in places, a crust of dark green phyllite-like rock, up to 1 cm thick, in which separate nodules are submerged. The matrix has a thin-laminated texture. The microscale interrelation between the nodules and the matrix (Fig. 1) resembles postsedimentary compaction structures in clay rocks containing diagenetic nodules (Gavrilov, 1982). In the thin section, the color of the matrix changes from pale yellow to dense green, with clear pleochroism in a green tint. The yellow tint, in some sectors, more likely suggests pigmentation with iron oxides. This rock has the approximate bulk chemical composition of basalts ($\text{SiO}_2 < 50\%$) with a higher loss on ignition (relative to fresh basalts) (Table 1; Sample M-232-10a). Based on the powder diffractometer pattern, the phyllitic substance is made up of Fe-chlorite (sharp increase of II order basal reflections) with a quartz and mica admixture. An admixture of other minerals in the studied specimen is negligible, although fine pumpellyite-bearing fractures are seen in thin sections. Aside from this, the chlorite material includes chains of magnetite (titanomagnetite?) microcrystals.

All nodules from the jaspers of the discussed lens are characterized by a regular zonal structure (Fig. 2). One can recognize in them a light-colored core (2–3 mm in diameter) and a bright red outer shell (1–1.5 mm thick).

The *core* includes chalcedony in the gray fine-spheroidal central zone. The siliceous mass is enriched in opaque, white (in reflected light) aggregates (globular leucoxene?). The outer part of the core is white-colored and also has a chalcedony composition, but it contains a much less amount of such inclusions, and is normally characterized by larger, divergently fibrous texture. In some larger spheroids, this part of the core is marked by the finest, well-seen concentric zoning, emphasized by the distribution of ore minerals (Fig. 3). Such a texture is typical of derivatives of autooscillation, including rhythmic reactions governed by diffusive phenomena in gels (Chukhrov, 1955). In this case, the formation of this texture resulted from the diffusion of oxygen and, accordingly, from the transport of an oxidation front from the surface of a gel blob toward its center. This process was accompanied by an accretion of metal oxides from the silica-gel mixture to each successive reaction sphere (according to the manner of Liesegang ring formation). The surface of the cores has an irregular shape, reflecting their inner spheroidal texture. The outermost part of the core shows a banded texture and is made up of an alternation of several parallel layers with a highly variable concentration of ore material. Such a texture is also presumably related to later rhythmic

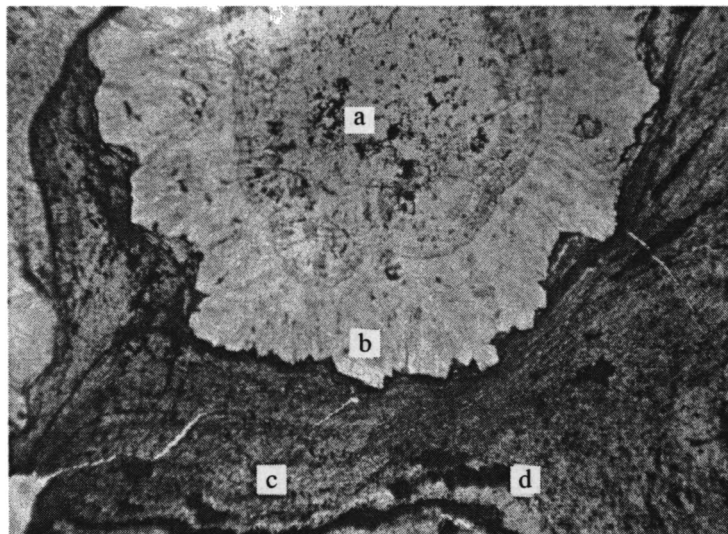


Fig. 1. Siliceous nodules in basal phyllite-like chlorite matrix at the base of a jasper body (thin section M-232-9, parallel nicols, magn. 40). (a) Chalcedony core (Ti-bearing ore segregations are dark); (b) lutecitic shell (rhombohedron faces of quartz, which replaces lutecite, situated on the outer surface); (c) green chlorite matrix; (d) magnetite chains.

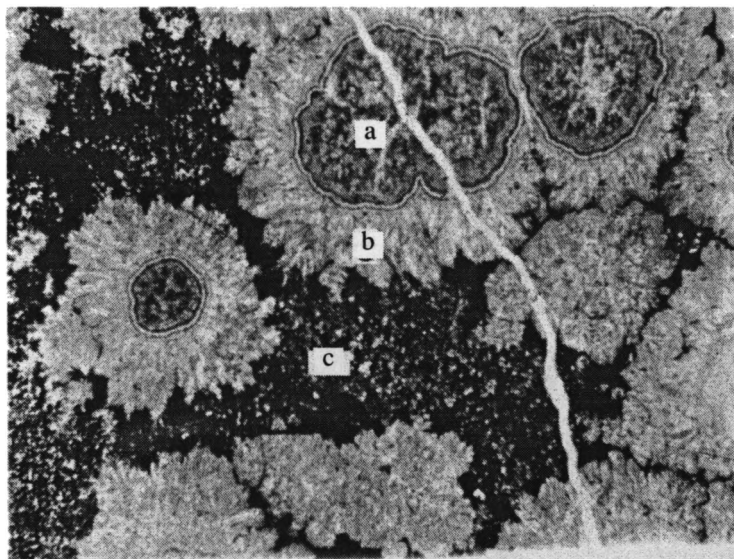


Fig. 2. Jasper with chalcedony-lutecite nodules and quartz-hematite matrix (thin section M-232-8, parallel nicols, magn. 14.5). (a) Chalcedony cores with Ti-bearing segregations confined to the inner part of nodules (the outer part of cores is banded and manifests rhythmic reactions in gel); (b) outer shell of nodules consisting of dendritic lutecite; (c) quartz-hematite matrix. Note the presence of nodules with two accreted chalcedony cores surrounded by a single lutecite shell.

mic oxidation reactions in a new portion of gel containing more ore component, as compared with the older gel. Syneresis joints are found in cores of large nodules.

The *outer shell* of the nodules consists of lutecite and has a chevron (flabellate) texture, emphasized by iron oxides. It is made up of divergent (dendritic) lutecite bundles enveloping the entire surface of a simple (one-drop) or complex core (Fig. 2). The latter may consist of several accreted chalcedony spheroids (initial gel blobs). In the above mentioned nodules, which are submerged in the basal chlorite matrix, i.e., located

near the contact with underlying lavas, one can observe pyramidal-faceted quartz "monocrystals" with relics of the initial fibrous lutecite texture (Fig. 1).

Submicroscopic crystals of hematite, which pigment lutecite and neomorphous quartz, are distributed along lutecite fibers, or form a specific moire pattern. The latter shows up as the alternation of pigmented and unpigmented (by hematite) concentrers, 5–6 μm thick (Fig. 4). The moire texture of a lutecite shell can be detected in many nodules. This suggests that the lutecite shell, similarly to the cores of the nodules,

Table 1. Content of major oxides (wt %) in nodular jaspers and host rocks

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total	CO ₂
M-232/10c	92.98	tr.	n.d.	5.17	0.27	tr.	n.d.	1.55	0.19	0.23	0.01	0.2	100.60	n.d.
M-232/10a	49.60	0.80	8.42	15.87	4.20	0.38	6.39	6.12	0.58	2.44	0.05	5.87*	100.65	n.d.
M-232/2	46.56	1.12	14.87	3.62	7.99	0.19	6.45	11.92	2.69	0.04	0.095	4.11	99.64	(0.02)
A-68/1a	88.20	tr.	n.d.	8.45	0.68	0.06	0.40	1.43	0.19	0.20	0.00	0.77*	100.38	n.d.
A-68/1c	93.07	tr.	n.d.	3.92	0.31	0.03	n.d.	1.67	0.19	0.18	0.01	0.16*	99.54	n.d.
C-2329/8	89.89	0.10	0.72	3.00	0.22	0.02	n.d.	3.71	0.07	0.05	0.01	1.67	99.45	(1.10)
C-2329/12	50.27	1.32	12.32	4.93	8.65	0.21	7.20	8.11	4.55	0.16	0.06	2.59	100.37	n.a.

Note: (M-232/2) tectonically crushed basalt; (C-2329/12) pillow basalt; (M-232/10a) phyllite-like green rock at the base of nodular jaspers; the rest of samples are nodular jaspers. (tr.) traces; (n.d.) not detected; (n.a.) not analyzed. (Contents within the parentheses are not included in the total sum of oxides.) Values of loss on ignition, marked by asterisk, correspond to sum of H₂O⁺ and H₂O⁻.

retained traces of rhythmic reactions in a ferruginous-siliceous gel. The initial composition of iron oxides in the gel remains problematic, although now they are represented by hematite.

The major constituent of the basal and filmy matrix of nodules is hematite and granular quartz. As compared to ore particles pigmenting lutecite, the hematite forms relatively large flakes.

Area 2 is located in the divide of the Vaamochka and Podgornaya rivers. Here, N.Yu. Bragin took a sample of red nodular jasper (observation point A-68). It forms a lenslike body among basalts in the Upper Permian effusive-siliceous sequence composing one of the

Ekonai Terrane slabs. The length of the lens and its thickness are about 1 m and a few tens of a centimeter, respectively. The texture of the jasper is variable. Differences concern the dimensions of the nodules and, first of all, the quantity of internodular matrix. There are sectors consisting of bright red compact nodules (1–3 mm in size) or larger (up to 8 mm) bright red nodules floating in a dark ferruginous (predominantly hematite) matrix.

In contrast to type 1 nodules from the previous area, type 2 nodules in jaspers under consideration do not have a chalcedony core, and the siliceous component of the whole nodule is represented by lutecite. The central



Fig. 3. Rhythmic banding in small spheroids composing chalcedony cores of nodules (thin section M-232-9, parallel nicols, magn. 400).



Fig. 4. Section of lutecite shell with fine banding owing to rhythmic reaction (thin section M-232-9, parallel nicols, magn. 400).

part of these nodules (core) consists of fan-shaped (divergent) bundles of lutecite pigmented with hematite (Fig. 5). The most pigmented, outer part of the core often includes a thin hematite-rich shell. The lutecite cores or aggregates of initial spheroids are normally surrounded by a well-defined hematite shell, 0.2–0.3 mm thick, which is not intersected by lutecite bundles. Its formation was likely a consequence of the removal of iron compounds from the initial cores, which are quickly formed around the centers of crystallization. The growing iron oxide shell increasingly hindered the link of lutecite cores with the ambient solution, hampering the accretion of silica and terminating the growth of lutecite bundles. Prior to this, separate cores were able to stick together.

Segments of the jaspers between the initial single-spheroidal or polyspheroidal lutecite nodules, coated by hematite, are characterized by an accretional layered texture. In thin sections, one can observe that the core is surrounded by an alternation of thin fringes, which consist of small hemispheres of newly formed lutecite bundles, and hematite shells (Fig. 5). Such a structure reflects the continuing oscillatory process of lutecite nodule formation. It was controlled, on the one hand, by the displacement of iron oxides from new zones of the lutecite accretion, and, on the other hand, by the suppression of their growth, when the ferruginous coating attained a certain thickness, and a new cycle started.

Radial joints develop inside large nodules. These joints are filled with granular quartz and pinch out toward the surface of the nodules (Fig. 5). They resemble syneresis joints in septarian nodules and may indi-

cate the participation of gels in the formation of the nodules. Probably, in this case, the initial solution remaining between lutecite bundles was coagulated. Later joints, completely cutting the rock, are also observed. They associate with quartz and calcite, suggesting that the rock was subject to later processes similar to those observed during retrograde epigenesis.

Area 3, from which S.D. Sokolov took a sample of bright red nodular jasper, is located in the southeast of the Taigonos Peninsula (observation point S-2329/8). The accretion structure of this sector of the peninsula is composed of a tectonic melange of ophiolite complex and fragments of oceanic effusive–sedimentary rocks. For a long time, they have been attributed to the single Kingiveem Formation. Investigations carried out during the last years showed that in the Taigonos Peninsula, as in the Penzhina Ridge, the Kingiveem-type sequence includes Upper Triassic, Jurassic, and Tithonian–Lower Cretaceous effusive–siliceous complexes (Bondarenko and Sokolov, 1996; Konstantinovskaya, 1998; Vishnevskaya *et al.*, 1998). They make up four tectonic slabs separated by outcrops of the serpentinite melange.

Nodular jasper is found in one of the slabs (Kingiveem-1) among the Tithonian–Berriasian part of the sequence. The jasper represents a thin crust on the surface of pillow-basalts, at the boundary between the basaltic flow and the overlying radiolarites. The size of nodules is up to 2 mm. By their structure they resemble nodules in area 1 jaspers. They also have a chevron texture and are composed of dendrite-like, radiating bundles of lutecite (Konstantinovskaya, 1998; Fig. 6).

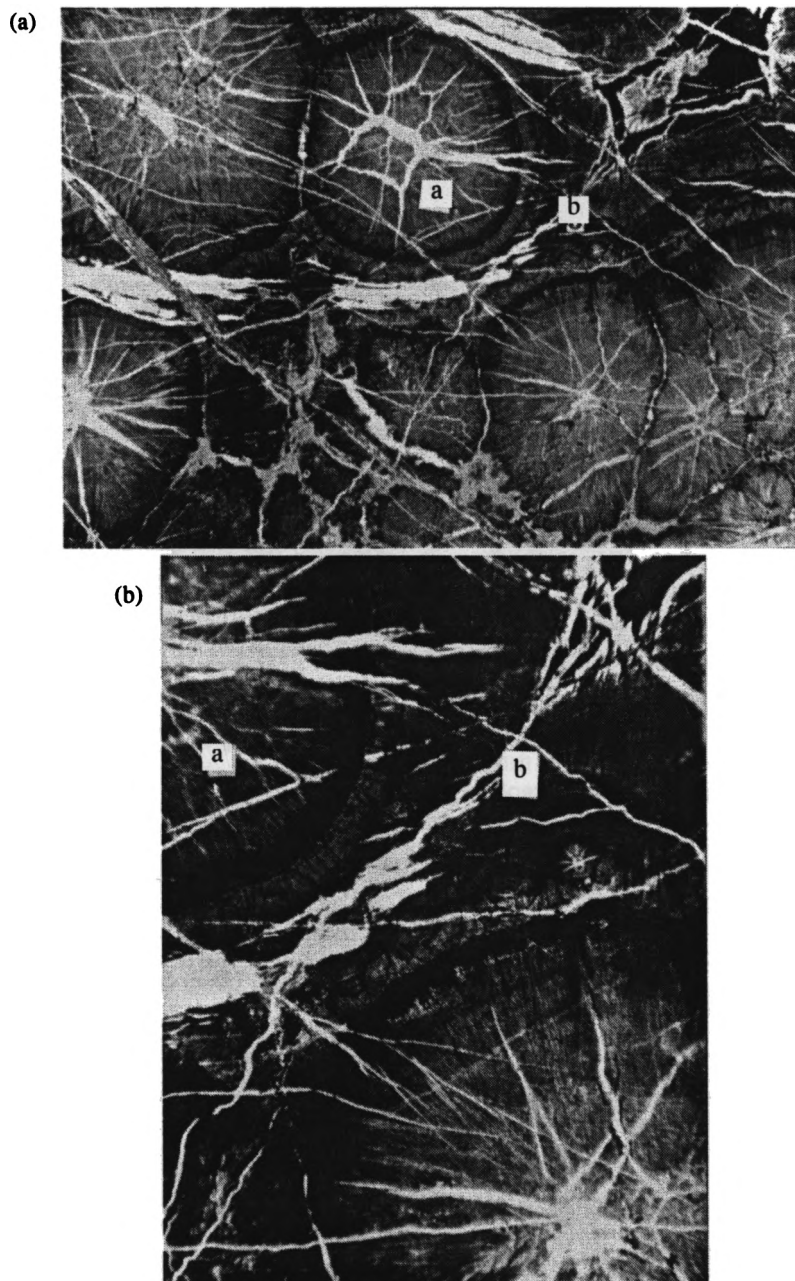


Fig. 5. Jasper with lutecite nodules (thin section A-68-b, parallel nicols, (A) magn. 14.5, (B) the same, magn. 40). (a) Lutecite spheruloids of the first generation bounded by a hematite rim that terminated the growth of initial crystals; syneresis joints are widely developed in nodules; (b) accretionary lutecite-hematite pair rims on initial spherulites or on aggregates of accreted initial spherulites; alternation of lutecite and hematite shells of a later generation is seen; (c) cavities filled with youngest hematite segregations and separate quartz grains.

At the same time, chalcedony cores remain unestablished in them (it is conceivable that they were smaller in size and, hence, are poorly preserved). The rock is brecciated, and, as a result, a portion of the nodules is crushed, acquiring a sand-silt size. They were mainly crushed along the boundaries of differently directed bundles of lutecite. Some of these fragments are slightly calcitized, probably due to retrograde epigenesis.

CHEMICAL COMPOSITION AND GEOCHEMICAL FEATURES OF JASPER

The chemical composition of all studied samples of nodular jaspers is characterized by a high content of SiO_2 (>90%) and increased content of Fe_2O_3 (3–9%), relative to other major components (Table 1). The CaO content exceeds 3% only in Sample C-2329-8, in which epigenetic calcitization is displayed in fissures. Nor-

Table 2. Content of REE (ppm) in nodular jaspers and host rocks

Sample	La	Ce	Nd	Sm	Eu	Tb	Er	Yb	Lu	Ce_n/Ce_n^*	Eu_n/Eu_n^*	La_n/Sm_n	La_n/Yb_n
M-232/10c	0.13	<0.5	<0.5	0.11	0.033	0.037	n.d.	0.21	0.046		0.86	0.15	0.04
M-232/10b	0.91	3.15	1.55	0.6	0.2	n.d.	0.91	1.05	n.d.	1.08		0.18	0.06
M-232/10a	2.2	5.0	4.8	1.8	0.72	0.58	n.d.	2.5	0.37	0.57	1.21	0.19	0.07
M-232/2	2.9	8.2	7.8	2.7	0.98	0.65	n.d.	2.7	0.40	0.62	1.34	0.16	0.08
A-68/1a	0.33	0.76	0.55	0.13	0.036	0.03	n.d.	0.20	0.035	0.72		0.35	0.11
C-2329/8	0.38	0.97	0.65	0.2	0.057	0.088	n.d.	0.380	0.054	0.80	0.69	0.28	0.07
C-2329/12	2.7	7.9	6.3	2.4	0.85	0.58	n.d.	2.4	0.37	0.74	1.31	0.16	0.08

Note: $Ce_n/Ce_n^* = 2Ce_n/[La_n + Nd_n]$, $Eu_n/Eu_n^* = 2Eu_n/[Sm_n + Gd_n]$ are Ce and Eu anomaly contents respectively, normalized to the PAAS (Post-Archean Australian Schist). See Table 1 for the rest of denotations.

mally, it is not more than 1.5%, and, judging by the absence of carbon dioxide in analyses, it is not related to the carbonate admixture. The quantity of other oxides in jaspers does not exceed a few tenths of a percent. The very low total content of REE (up to 10 ppm) is a characteristic feature. This is unusual for other siliceous rocks from the host complexes (Table 2). The REE distribution in nodular jaspers is analogous to that in the host MORB-type tholeiite. As in basalts, they are enriched in HREE relative to LREE (Fig. 6). This is clearly seen from the PAAS-normalized ratio of La_n/Sm_n (0.22–0.28) and La_n/Yb_n (0.06–0.07). By their geochemical parameters, nodular jaspers sharply differ from overlying radiolarites, for which the typical variations of oceanic pelagic sediments in REE distribution are recorded (Konstantinovskaya, 1998). Investigation of geochemical peculiarities in radiolarites, clay jaspers, and siliceous mudstones, associated with effusives in the accreted oceanic volcanogenic-sedimentary complexes of the Koryak–Kamchatka Fold Belt, gave the following result. Like present-day oceanic sediments, they normally show either (1) differential hydrogenic spectra of REE distribution with negative or positive Ce anomalies (related to geochemistry of deep oceanic waters, sedimentation rate, and correspondingly, sediment exposure duration), or (2) weakly differential spectra (equalized relative to the PAAS), which are similar to those observed in many types of pelagic mud and primarily reflect the contribution of allothigenic aluminosilicate admixture. Like the mineral composition, the sharp fractionation of HREE, relative to LREE within one or one and a half order of magnitude (Fig. 6), is an important distinction of the studied nodular jaspers from biogenic siliceous rocks of this association. The tholeiitic spectrum of REE distribution and the absence of signs of the positive Eu anomaly, which is typical of solutions supplied to the seafloor in the discharge zones of large hydrothermal systems (Butuzova, 1989, 1998), more likely testify to the formation of nodular jaspers as a result of chemogenic precipitation of siliceous sediment from the hot solution of a peculiar type.

CRYSTALLOOPTICAL MODELS OF THE MAIN VARIETIES OF FIBROUS QUARTZ

Before approaching the problem of formation for the above-described nodular jaspers, it is necessary to dwell on the peculiarities in structure of the main varieties of fibrous quartz. Three of its varieties are best known: length-fast chalcedony (with negative elongation of fibers), length-slow chalcedony (quartzine with positive elongation of fibers), and lutecite (with oblique extinction of fibers). In publications written in English, lutecite is also often described as length-slow chalcedony. In addition, in papers not dealing with mineralogy, all types of fibrous quartz, until now, were usually designated as chalcedony (Khotin, 1976), or chalce-

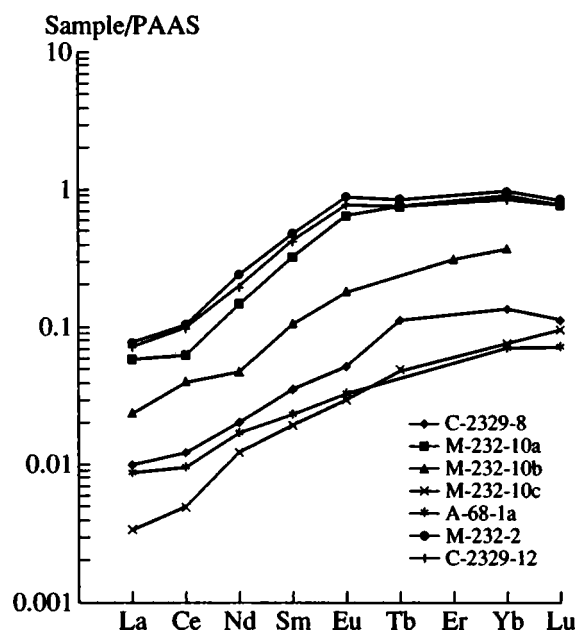


Fig. 6. Spectra of REE distribution normalized to the PAAS (McLennan and Taylor, 1981) in nodular jaspers and associated basalts. Sample numbers correspond to those listed in Tables 1 and 2.

donic quartz (Keene, 1983). This general term implies only the presence of fibrous texture.

Fibrous varieties of quartz are still not clearly understood because of their cryptocrystallinity. Nevertheless, the structure of chalcedony and quartzine can be characterized thanks to works by Braitsch (1957), Correns and Nagelschmidt (1933), and Frondel (1978). On the basis of these works, Murav'ev (1989) proposed a crystalloptical model of chalcedony as a multitude of quartz crystallites, joined in fibers that are oriented parallel to $[11\bar{2}0]$ and $[10\bar{1}0]$, with an equally probable rotation of individual axes of separate crystallites in planes normal to the direction of the fibers. In this model, the value of np of chalcedony (np_{chal}) must theoretically be equal to the np of quartz (np_q), but the ng of chalcedony (ng_{chal}) is lower than the ng of quartz (ng_q), because the latter reflects the cumulative effect of ng' from a plethora of quartz crystallites rotated relative to each other at angles of 0 to 90°. In any plane parallel to fibers, ng_{chal} is defined by the projection of ng of quartz crystallites, which are rotated relative to the axis of fibers, onto this plane (i.e., it is dependant on the cosine value of the slope angle relative to the plane). In this case, the ng_{chal}/ng_q ratio must be the same as the diameter/length ratio of the corresponding semicircle, at a tangent to which quartz crystallites of chalcedony are oriented. This ratio is 0.64. Under such conditions, the birefringence of chalcedony must naturally be $0.64x = 0.0057$, where x is the birefringence of quartz (0.009). The possibility for instrumental checking of this figure with the help of a Berek compensator allows us to estimate the correspondence of the presented crystalloptical model of chalcedony to the real pattern. The birefringence was studied in a single thin section in order to eliminate the effect of different thicknesses, and the real value of birefringence for the Syrian chalcedony (0.0054) turned out to be close to the calculated one. Thus, the data obtained from the Syrian chalcedony showed the validity of the discussed model of the chalcedony structure.

The structure of lutecite for a long time has been the least discussed in publications. Based on the data obtained, with the use of nannopetrography and optical petrography, Murav'ev proposed in the same paper a model according to which lutecite fibers are elongated along one of the faces of rhombohedrons bounding equidirectional lamellar quartz crystallites of the fibers (Murav'ev, 1989). Accordingly, axes of these crystallites must be unidirected at an angle of 38° to the direction of fibers. Some areas in lutecite, indeed, show extinction angles of 38°, which corresponds to slope angle of rhombohedron faces relative to the crystallographic axis of quartz. Before this, the maximum extinction angle for lutecite was indicated in handbooks as 30°, because the measurements were generally carried out on accidental shear planes of thin sections.

In the paper cited above, it was emphasized that lutecite is characterized by sufficiently large, microscopically observable bundles of fibers with a common crystalloptical orientation of submicroscopic quartz crystallites, not only within each fiber (as in quartzine), but also in some volume. Such a structure explains why only the lutecitic variety of fibrous quartz sometimes serves as a nucleus for the successive overgrowth of the quartz monocrystals. In this process, the nucleus relieves preserve the initial fiber orientation, which does not coincide with the direction of the crystallographic axis of newly formed quartz, but is parallel to the face of rhombohedron. The chevron texture typical of lutecite nodules can also be explained by structural peculiarities of lutecitic bundles and their orientation relative to each other.

The hypertrophied development of faces of the rhombohedron in quartz lamellas, composing lutecitic fibers and bundles, gives the opportunity to consider these bundles as peculiar skeletal crystals.

SOME PROBLEMS IN THE FORMATION OF THE STUDIED NODULAR JASPER

Three groups of problems are related to the origin of the jaspers discussed above. The first group concerns the general assessment of conditions, under which the formation of each nodular jasper deposit occurred. The second one concerns the origin of SiO_2 -rich solutions. The third group embraces purely mineralogical questions related to the mechanism of crystallization for different types of fibrous quartz, and the elucidation of the role of separate physicochemical parameters in this process. Although all these problems are closely interrelated, some aspects regarding the origin of fibrous quartz varieties have independent importance, and their comprehensive analysis needs the involvement of additional factual data, including those related to genetically different objects. In the presented paper, conclusions on the formation of both chalcedony and lutecite are related, first of all, to specified deposits and samples. It is possible that this problem may be more thoroughly discussed in a special paper devoted to the genesis of fibrous quartz varieties.

The clear paragenesis of the jaspers under consideration with basalts is hardly an accidental occurrence. Their usual location in sequences, namely, in the upper parts of basalt flows and at the boundary of the basalt with pelagic sediments is beyond question. Therefore, we believe that the formation of these jaspers could hardly be separated for a long time span from submarine lava effusions. The small size of nodular jasper deposits and their dispersion among other rocks of the formation testify that the precipitation of initial siliceous sediments was local and not related to discharge sites of large hydrothermal systems. The formation of SiO_2 -rich thermal solutions in the cases under review seems to have been related to processes within one or several lava flows of a single eruption. The structure of

lava flows (pillows and tubes) on the oceanic floor is favorable for the entrapment and partial isolation of near-bottom water in lava cavities. As a result of heating, the water can actively react with the cooling rocks.

In our case, the most plausible model showing the formation of Si-bearing thermal solutions is based on the interaction of basaltic glass with seawater at elevated temperatures. The study of different natural objects recovered by deep-sea drilling on the seafloor of present-day oceans and exposed in the fold belt framing, as well as the results of special experiments, attest to the fact that the contact zone between fresh volcanic (primarily basaltic) glasses and seawater is characterized by an active exchange of elements, leading not only to alteration of the glasses, but also to the prominent metamorphization of the captured water.

In experiments carried out under increased temperatures, when the quantity of seawater with normal salinity (0.13% Mg) was tens of times higher than the quantity of crushed basaltic glass placed in an autoclave, its alteration had a greenstone trend. This was reflected in changes of the bulk chemical composition of the rock with an increase of MgO content (Mottl, 1983). During the experiments (duration from 25 to 602 days) carried out within a temperature interval of greenschist facies (250–450°C), the change of mineralogical composition of basalts was expressed in the formation of smectites and smectite-chlorites. Although the formation of chlorite during the indicated time span was detected in none of the experiments, according to the suggestion of Mottl (1983), such a process led to the origination of MORB rock replaced by chlorite. If so, we should admit that the rate of the successive replacement of glasses with layered minerals of the "greenstone" affinity toward the well-crystallized chlorites at temperatures above 250°C significantly increases, as compared with that observed during the catagenesis of volcanic glass in Pacific cover tuffs and coeval rocks of its rim (Grechin, 1987).

In respect to the origin of nodular jaspers, the thermal submarine alteration of basalts is of interest, because it is commonly accompanied by the escape of Ca, Fe, Al, Mn, etc., and SiO₂ from glasses to ambient seawater. It is well known that temperature is the main factor of SiO₂ solubility increase. With an increasing temperature, from 25 to 250°C, its solubility per kilogram of solution increases from 130 to 1120 mg for amorphous forms, and from 9 to 500 mg for quartz (Holland, 1970). Thus, the potential possibility of SiO₂ dissolution in seawater captured by lavas sharply increases only due to its heating. This gives an opportunity for this water, which interacts with basalts, to be metamorphosed and transformed into a thermal solution with a high concentration of SiO₂. The experiments on the interaction of basaltic glasses with seawater under an increased temperature and pressure show that, indeed, at a temperature of 250–300°C, the SiO₂ content in the solution rises in several days by a factor of

25–30, as compared with its concentration in seawater (Seyfried and Mottl, 1982).

In these experiments, the extraction of Mg from seawater during the formation of secondary silicates was accompanied by a sharp drop of pH from 7.5 to less than 3 (measured at a temperature of 25°C at the end of each experiment). This is explained by the fact that Mg²⁺ from seawater is consumed for the smectitization of glass in the form of Mg(OH)₂, whereas H⁺ remains in the solution for some time (Bischoff and Dickson, 1975). At such low pH, the mobility of Fe dramatically increases. The transition of Fe²⁺ into insoluble oxide forms occurs at significantly higher (positive) values of Eh (Garrels and Christ, 1968). Aside from this, under such ultra-acidic conditions, many other elements (e.g., Al and Ti) also become mobile.

We suppose that, during basaltic extrusions on the seafloor, some cavities inside lava flows were frequently filled with acidic thermal (metamorphogenic) solutions, which were newly formed at the expense of seawater. These solutions were rich in SiO₂, Fe, and other elements. Although the REE behavior was not studied in the experiments, it is probable that, in the process of redistribution of elements during glass transformation, part of the rare earth elements passed into the solution. The above-mentioned specific geochemical characteristics of nodular jaspers indicates that REE passed into the solution but retained the interrelations typical of host basalts. Taking into consideration that the background REE content in seawater is very low, these elements could not appreciably influence geochemical characteristics of the metamorphogenic thermal solution.

As for the deposition of silica from such solutions and the subsequent formation of nodular jaspers, the factual data cited above suggest that the ways of their formation were different for separate jasper deposits and could be governed by different parameters of solutions: temperature, cooling conditions, and the style of interaction with near-bottom seawater, leading not only to a temperature fall and the corresponding decrease in solubility of all forms of silica, but also to their neutralization as a result of the mixing.

The genesis of jaspers found in exposure M-232 is of particular interest. Their formation was related to eruption onto the seafloor of acidic, hot solution rich in Al, Fe, and SiO₂. The probable relatively high density of this solution (relative to seawater) dictated its accumulation in the nearest depression on the lava surface, where different X-ray-amorphous phases were successively precipitated.

The above-discussed structural-mineralogical peculiarities of jaspers from this deposit show that its formation can be divided into several stages differing in composition and specific features of crystallization of siliceous sediments. At stage 1, characterized by the mixing of the solution with near-bottom water at falling temperature and rising pH, the ferruginous aluminosil-

icate gel was precipitated and transformed into chlorite. The continuing steep drop in temperature, under direct contact of the solution with near-bottom water at stage 2, enhanced further polymerization of SiO_2 ions, transition of the solution into a colloidal form, and precipitation of the initial siliceous gel from it (in the absence of alumina). Its subsequent crystallization led to the formation of chalcedonic cores of nodules (stage 3). The spheroidal shape of chalcedonic cores reflects the appearance in the original gel of forces of surface tension, which is known to be very typical of many colloidal sediments (Chukhrov, 1955). Forces of surface tension acted at boundaries between initial gel blobs and the ambient residual solution. Under such conditions, the above-noted blobs, at the first stage, already had a rounded shape. The location of the largest nodules at basal parts of the lens and the presence of nodules with polyspheroidal chalcedonic cores are likely to be explained by the initial gravitational differentiation of blobs in the residual solution.

Previously, on the basis of completely different factual data, Murav'ev (1983) noted that the distribution of stress during gel-drop dehydration and crystallization probably predetermined the trend toward the tangential orientation of crystallographic axis of the growing quartz crystallites in chalcedony and the appearance of syneresis microjoints in aggregates in accordance with the directions of tensile stress. A high content of water, even in consolidated siliceous gel (over 70%), leads to sufficient reduction in volume during gel crystallization. Consequently, the geometry of contraction forces is best manifested in fibrous chalcedonic aggregates forming from gel blobs in the appearance of both radial fibers and concentric spheres that simulate the shape of blobs and sinters (Murav'ev, 1989). Such a growth scheme explains that the structure of chalcedonic spherulites is emphasized by radial and concentric systems of alternating bands. This scheme of chalcedonic spherulite formation is not in serious contradiction with that observed in nodule cores from the jaspers under consideration. The differences between the inner and outer parts of nodule cores seem to be explained by two stages of coagulation in the primary solution. They differed at least by the content of ore admixture (presumably leucoxene micrograins, based on thin sections) in gels. Probably, the outer part of the cores originated from a new gel portion that precipitated during the cooling and coagulation of the residual colloidal solution that surrounded the primary blobs of siliceous gel.

The next, probably syncontemporaneous, stage of jasper formation (stage 4) was characterized by the formation of lutecite shells. The crystalloptical model of lutecite discussed above suggests that it was formed according to the scheme of the growth of skeletal crystals, i.e., a significantly faster growth of rhombohedral faces of quartz (relative to prismatic faces) at increased temperatures (kinetic effect). The formation of skeletal crystals is a characteristic process for the crystallization of oversaturated solutions. In turn, gradual changes of

certain parameters influencing solubility are favorable to the origin of these solutions. In our case, the lutecite most likely precipitated under conditions of a later, less sharp (as compared to that at the earlier stages) decrease of temperature in the solution that was already depleted in earlier stages. Under such conditions, the SiO_2 concentration attained the limit of quartz solubility, but did not reach the values needed for the precipitation of amorphous phases. As soon as the solution became somewhat oversaturated (relative to quartz solubility), lutecite could precipitate. The primary gel blobs were likely crystallization centers that enhanced the almost instant overgrowth of lutecite bundles. The lutecite-hematite paragenesis indicates that, at the stage of its formation, the siliceous solution was enriched in iron oxides. The main reason for the beginning of the precipitation of iron oxides was most probably the ongoing solution neutralization by seawater under near-bottom oxidizing conditions.

During the last stage of formation for this type of jaspers (stage 5), the central parts of internodular spaces were filled with granular quartz. This process probably represented a slower and more prolonged precipitation from undersaturated solutions. The role of the kinetic effect, which was important during the formation of fibrous quartz varieties, was suppressed at this stage by limited resources of the solution and, correspondingly, by the slow supply of the "structural material" (SiO_2). It is possible that the deceleration of quartz precipitation was responsible for the relative enrichment of the central parts in hematite. The precipitation of iron hydroxides was probably the main process leading to the sorptive extraction of REE from the solution.

At the postsedimentary stage, rocks of the deposit were not metamorphosed, as indicated by the preservation of chalcedony. The alterations were restricted to a pumpellyite grade of early metagenesis (according to the nomenclature proposed by Kossovskaya and Shutov, 1971). The retrograde epigenesis was noted by a patchy (very intensive in places) calcitization of rocks. It mostly affected the broken basaltoids.

The genesis of the nodular jaspers from the A-68 deposit, situated among basaltic lava, probably differed from that of the M-232 type by an absence of the sharp-drop-in-temperature stage of the solution, when the SiO_2 content instantaneously reached the limit of solubility of its amorphous forms. The cooling was gradual, and the solution became oversaturated (relative to quartz) at a certain stage. The jasper formation started directly with the precipitation of initial lutecitic spheroids around embryonic centers of crystallization. The precipitation of lutecite prevented the silica concentration in the solution from reaching the limit of solubility of amorphous silica. The precipitation of initial lutecite spheroids seems to have been accompanied by gravitational floatation of relatively small lutecitic nodules above the rest of the solution enriched in iron oxides,

where larger and more complex nodules with polyspheroidal cores were formed. During the formation of such nodules, the precipitation of lutecite proceeded as pulsations. The growth of lutecite stopped as soon as the shell of iron oxides, expelled from the crystallized part of nodule, disturbed its link with the rest of the solution. The accretion of layers of a new, ordinary lutecite–ferruginous lutecite pair began, but each time it took place from a lesser volume of the solution. Segments with traces of rhythmic reactions, observed in separate nodules, as well as syneresis joints, can be explained by assuming that the initial lutecitic aggregates had a high porosity and were filled with residual, subsequently gelified, ferruginous–siliceous solutions.

The last stage of the formation of jaspers under study was similar to that for the previous type of jasper; i.e., it was characterized by the precipitation of the major hematite and the subordinate granular quartz.

The formation of the nodular siliceous crust, found at observation point S-2329/8, seems to have occurred, as in the first case, at the contact between the solution and near-bottom water, but the temperature difference was not very high, and the solution was more depleted. The limited field observations do not allow a more detailed characterization of formational conditions of this type of jasper.

CONCLUSION

The investigations carried out showed that specific (in mineralogical and geochemical composition) chemogenic nodular jaspers are encountered in the upper parts of lava flows and at their boundary with overlying rocks of effusive–siliceous sequences accreted in fold belts of the northwestern rim of the Pacific. Lutecite, a fibrous variety of quartz with an oblique (up to 38°) extinction of fibers, is characteristic of these jaspers. In the studied samples, it composes either entire nodules or their shells. In the last case, the inner cores of nodules are made up of chalcedony. In sequences recovered in deep-water boreholes in the northwestern Pacific, siliceous segregations with lutecitic composition occupy an analogous location at the boundary of lavas and sediments (Keene, 1983).

We suggest that the jaspers discussed in this paper are typical derivatives of an unbalanced system arising at the contact of seawater and basaltic lavas on the seafloor. They are the products of water–rock interaction that was almost syncontemporaneous with the effusions and was marked by relatively high temperatures of cooling lavas (in contrast to the subsequent process of halmyrolysis).

Other varieties of fibrous quartz, first of all quartzine, were not found in the studied jaspers, probably because our jaspers were formed as a result of the cooling of hot solutions. This is in agreement with the data by Keene (1983) indicating that quartzine in oce-

anic basalts appear in association with barite and carbonates, i.e., in lower temperature mineral parageneses.

We suggest that solution temperatures and the pattern of their cooling were the main factors controlling the mineralogical composition of the described nodular jaspers.

The Paleozoic–Mesozoic age of jaspers raises a question: to what extent do their modern mineralogical compositions correspond to the initial one. Normally, during the crystallization of siliceous gels (including those from sediments of present-day caldera lakes), the initial formation of metastable phases of silica (tridymite and cristobalite) is noted. This resembles the opal → opal-CT → quartz succession of catagenetic transformations in biogenic siliceous sediments from the Pacific sedimentary cover and in sequences exposed in its continental rim (Grechin, 1996). At the same time, the experiments carried out by Oehler (1976) on crystallization of siliceous gels under hydrothermal conditions, showed the following: in all cases, within an interval of 100–300°C and at a pressure of 3 kbar, quartz modifications of silica were immediately formed, whereas transitional phases of silica were not recorded. The explanation of this should be searched for in the kinetics of growth of a specific phase of silica. One can suppose that the structure of silica polymers in colloids and factors influencing the structure determined the mineralogical trend of the subsequent crystallization of siliceous gel, in particular, the formation of primarily metastable or immediately stable phases. However, this problem needs special investigation. It is probable that during the formation of nodular jaspers, as in the experiments on the crystallization of gels, chalcedony precipitated immediately.

It should be emphasized that the REE distribution in the studied nodular jaspers turned out to be anomalous for most sedimentary rocks, and, as was shown, they inherited the MORB-type distribution observed in host basalts. The simplest explanation of this fact is the alleged formation of solutions due to the metamorphization of seawater captured by lavas and the removal of REE from basaltic glass without the disturbance of the REE distribution pattern.

Solutions, which produce jaspers similar to those described above, are related to local, shallow submarine hydrothermal systems affecting a few lava flows of a single eruption. These solutions differed dramatically from the ore-bearing thermal solutions related to the discharge of deep-seated hydrothermal systems revealed recently in seas and oceans (Butuzova, 1989, 1998). The small size of nodular jasper bodies suggests that the quantity of silica removed from basaltic glass was sufficient for their formation. This silica was extracted during smectitization of the surface layer of cavity walls, through which the seawater captured by submarine lava flows percolated. The confi-

dent identification of traces of this initial smectitization in ancient metabasalts is in all probability an insoluble problem.

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Relations between Hydrothermal Mineralization and Seismicity of Mid-Oceanic Ridges

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Abstract—Regular relations in the distribution of earthquake epicenters and location of present-day hydrothermal fields along mid-oceanic ridges (MOR) were previously noted by a number of investigators; however, their origin and character have not been clarified so far. Despite restrictions due to inadequate study, the joint consideration of seismicity and hydrothermal mineralization of MOR makes it possible to conclude that it is necessary to distinguish several hierarchic levels or scales of investigation, since the character of these relations may be reversed depending on the scale. Five levels of MOR segmentation structures are conditionally distinguished. Whole ridges, whose boundaries are often represented by triple conjugations of plates (the coincidence of seismicity and mineralization zones, i.e., the direct correlation), belong to first order segments. Second order segmentation is most clearly expressed and consists in the division of MOR into rift areas (spreading centers) and transform fractures, the seismicity of the latter being higher, on average, by one order of magnitude (the inverse correlation). Rift areas are separated by nontransform displacements into smaller parts several tens of kilometers in size. The results of preliminary analysis for the East-Pacific Rise (EPR) and especially the Mid-Atlantic Ridge (MAR) show that, at the given hierarchic level, the direct correlation exists on the distribution of hydrothermal fields and earthquakes, owing to the coincidence of tectonically weakened and seismic zones. Further analysis is restricted to a few areas of the detailed study of microearthquakes with the help of local time networks. The sites of localization of increased seismicity, and active hydrothermal ore formation within segments of the fourth order, do not coincide because of the influence of thermal field inhomogeneities. The few works related to this problem suggest the volcanogenic and even hydrothermal nature of some earthquakes with small magnitudes within the hydrothermal field.

The systematic study of seismicity in oceans has been carried out for only a few decades. Still a shorter length of time (only 20 years) has elapsed since sulfide mineralization, connected with hot hydrothermal sources, was detected on the ocean floor. However, this period became a genuine revolution in the scientific and technical study of oceans. At present, there exist highly developed technologies for investigation of the hydrothermal activity of mid-oceanic ridges (MOR); on the other hand, numerous experiments on the study of oceanic earthquakes, in a wide interval of magnitudes, have been carried out. In most cases, these works have been accomplished independently and are almost autonomous. In fact, at first glance, the processes of ore formation and earthquake generation are incomparable. Nevertheless, their joint consideration is of certain scientific and practical significance. Both phenomena (hydrothermal ore formation and seismic activity) are in the final analysis the reflection of two leading processes (magmatism and tectonics) and, more exactly, their relationships. In contrast to the majority of continental deposits formed during tens to hundreds of millions of years, sulfide ores on the ocean floor literally appear before our eyes. Earthquakes are also a reflection of the modern dynamics of the lithosphere. The comparative simplicity of the geodynamic situation and

high intensity of tectonomagmatic and hydrothermal processes on MOR compensate to a considerable extent the briefness of their study and facilitate joint analysis. Therefore, the comparison of seismicity and ore occurrence distribution undoubtedly deserves attention.

The application of seismic criteria, along with other geophysical data, in prospecting for hydrothermal deposits was mentioned early in the work of Rona (1978). His observation was based on several facts of increased microseismicity in regions with intense hydrothermal activity. On continents, such observations were performed within the Rio Grande rift zone (Johnson and Combs, 1976; Quillan and Combs, 1976) and in the Imperial Valley, California (Combs and Hadley, 1977). In both cases, 5 to 70 microearthquakes per day, with a magnitude of <2.0 , were recorded. On the other hand, measurements in southwestern Iceland also indicated that the majority of microearthquakes occur at depths of 2 to 6 km, and spatially coincide with high-temperature hydrothermal systems (Ward and Bjornson, 1971; Klein *et al.*, 1977). An indirect relation of earthquakes in the ocean with magmatic and hydrothermal processes was also suggested on the basis of earthquake swarm observations in various parts of MOR (Francis, 1968; Sykes, 1970).

Recently, based on the distribution of earthquake epicenters over the Mid-Atlantic Ridge (MAR), Mazarovich and Sokolov (1998) arrived at the conclusion that hydrothermal fields gravitate toward relatively stable (aseismic) parts of rift zones. It is no doubt that the conclusion on the inverse correlation in the distribution of seismicity and localization of hydrothermal systems, is of great importance, in both theoretical and practical aspects. However, in our opinion, a more careful analysis is necessary here.

It seems that when comparing zonal distributions of increased seismic and hydrothermal activity, it is necessary to distinguish several hierarchic levels. We tried to accomplish the entire subsequent analysis precisely in this aspect. Our analyses were based on data from global seismic catalogs, such as NEIC (1963–1994, 8458 events with $m_b \geq 4.0$ over the 100-km zone around the MOR system) and CMT (1977–1995), as well as on the generalization of data on hydrothermal systems of MOR (Karta ..., 1988; *Gidrotermal'nye* ..., 1992). The total seismic moment over the observation period was used as a measure of seismic activity. The seismic moment of a separate event was assessed on the basis of the empirical formula $\log M_0 = 11.16 + 1.17m_b$, linking the moment and magnitude of body waves, for rift areas of the global system of MOR (Sobolev and Rundqvist, 1998).

Before proceeding to the description of results obtained, it is necessary to discuss the question as to what extent the available seismic data are representative. One of the substantial difficulties in the study of MOR seismicity is the remoteness of epicenters from the majority of recording teleseismic stations. The accuracy in determination of hypocenters is evaluated at 10–20 km and depends on the region; for example, in the Southern hemisphere, the error, as a rule, grows due to a thinner network of observations (Lillwall, 1982). Still worse is the situation with teleseismic determinations of depths. Reliable determinations of depths of strong events are rare, but they all indicate shallow-focus seismicity, usually not exceeding a depth of 10 km below the ocean floor. The earthquake recording level (the minimum reliably determined magnitude) is also different for various parts of MOR, and $m_{\min}$ varies, on average, from 4.5 to 5.0 (Drumya *et al.*, 1990). A near complete database, including epicenter position, seismic moment value, and mechanism, is contained in the Harvard Catalogue for comparatively strong earthquakes starting from 1977, however, the centroid depth of the seismic moment tensor cannot be determined for values less than 10 km. Observations by means of temporary seismic recording systems, mounted near the ridge, provided important results, however, only a small sector of MOR has been studied to date by such detailed works, and observation periods are comparatively small. Therefore, records of ground-level stations remain, as before, the main source of information about the seismicity of MOR as a whole. According to the available data, a stationary seismic regime is typical for

the majority of MOR areas (Lillwall, 1982; Boldyrev, 1994).

Thus, on the basis of teleseismic observations, we are able to seismically characterize MOR areas with dimensions exceeding 60–100 km. If seismic investigations are carried out on a larger scale, the accuracy of hypocenter determination will be insufficient, and the majority of earthquakes will be below recording level. These disadvantages can be eliminated by mounting temporary seismic stations near the ridge. At first, such observations were carried out on dry land in Iceland. Beginning in the 1970s, the number of investigations in oceans using acoustic buoys and bottom oceanic seismographs rapidly increased. Discussions concerning accuracy in the determination of hypocenter positions can be found in many works (Lillwall, 1982; Duchenets *et al.*, 1983). However, in any case, the accuracy has grown by approximately one order of magnitude, and the lower limit of magnitude has increased several-fold. The very first observations indicated that a large number of microearthquakes were registered within the boundaries of MOR even over comparatively short periods of observation. The basic results of early works performed in the Juan de Fuca Ridge and Mid-Atlantic Ridge areas allowed for more accurate determination of the position of the active ridge zone (Lillwall, 1982, and others) and focal depths. In the 1980s, the development of methods for comprehensive investigation of MOR by deep-water submersibles, special sounding acoustic systems, and geophysical methods resulted in the statement of new problems, such as the study of axial magmatic chambers, circulation of hydrotherms, and fracture formation near the ridge (Macdonald *et al.*, 1988). This also spurred seismic investigations, since it is obvious that the study of earthquakes was capable of providing important information on each of the specified problems. Most comprehensive works on the study of microseismicity were accomplished at two major sites—the central part of the Mid-Atlantic Ridge and the southern East Pacific Rise. However, as a rule, the dimensions of studied areas do not exceed 20–40 km, and their number as of yet is not more than 10. Therefore, on the basis of microseismic observations, the local structures of MOR can be, at present, characterized extremely fragmentarily for a number of sites on the MAR and EPR, although it is important to note that modern hydrothermal fields are located within boundaries of several such sites.

It is obvious that our knowledge about the distribution of hydrothermal mineral deposits within the boundaries of MOR at present is also extremely fragmentary and incomplete; today about 50 areas of distribution of sulfide ore occurrences are known. Since the study of MOR is very nonuniform, most attention has been concentrated on the two best investigated areas—the MAR between 12°N and 32°N and the EPR between 35°S and 15°N. Despite the nonuniform study of MOR, an intricate hierarchic organization of these structures with fractures of several orders and a regular

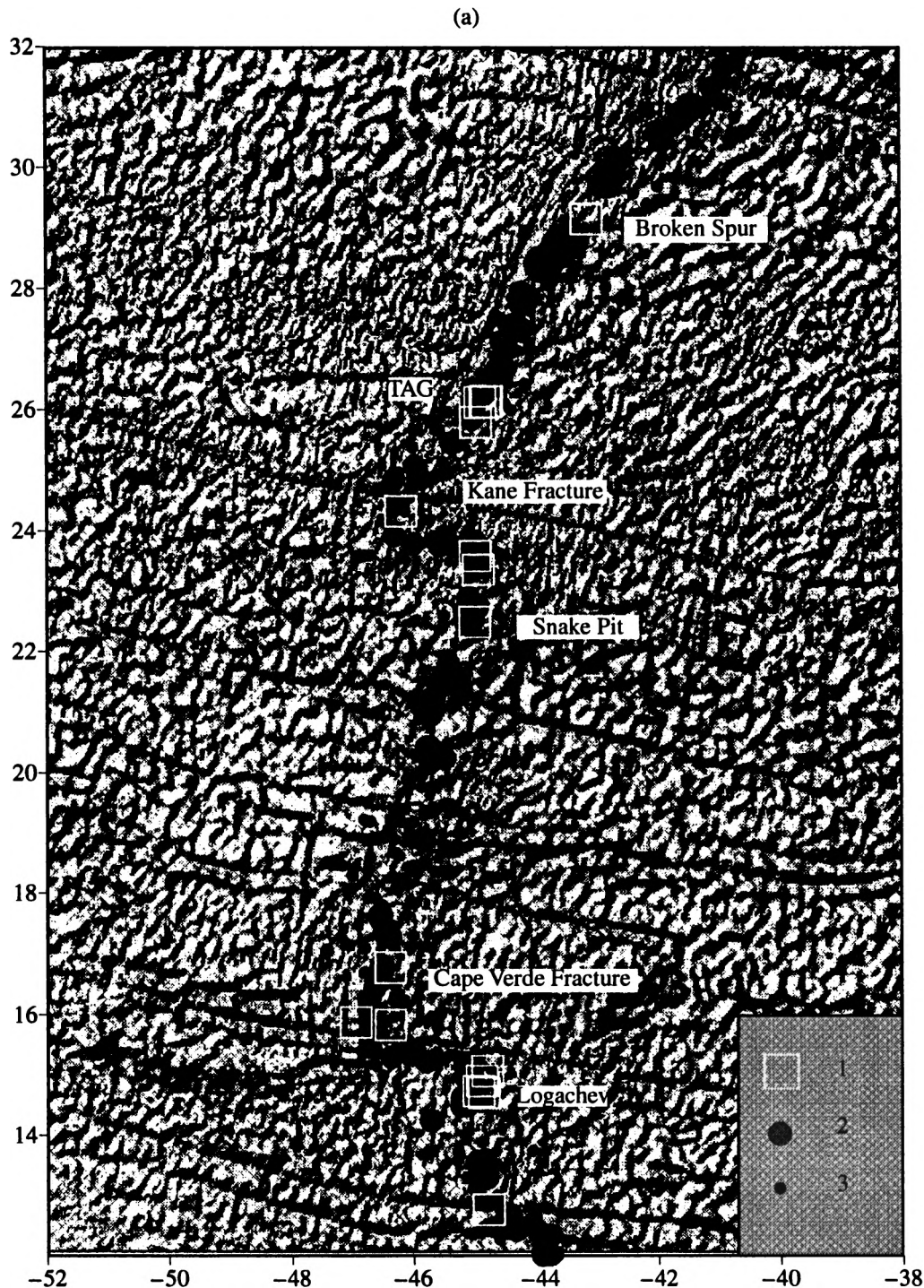


Fig. 1. Position of hydrothermal fields and epicenters for (a) the Mid-Atlantic Ridge and (b) the East Pacific Rise. (1) Hydrothermal fields; (2) earthquakes with $m_b \geq 5.0$; (3) earthquakes with $m_b < 5.0$.

localization of sulfide ore occurrences have been already proved today for the specified two structures. It will be shown later that similar regularities affect the distribution of MOR seismicity as well. Comparison of these two phenomena even at the given stage has made it possible to reveal quite regular relations, which will be undoubtedly refined in subsequent works.

As a first approximation, the zones of seismicity and hydrothermal mineralization in oceans coincide. The linear distribution of seismic activity in oceans was already noted by B. Gutenberg and Richter (1954). A virtually continuous global-scale distribution of earthquake epicenters along the MOR is clearly seen even on the map of Barazangi and Dorman (1969). One of the

(b)

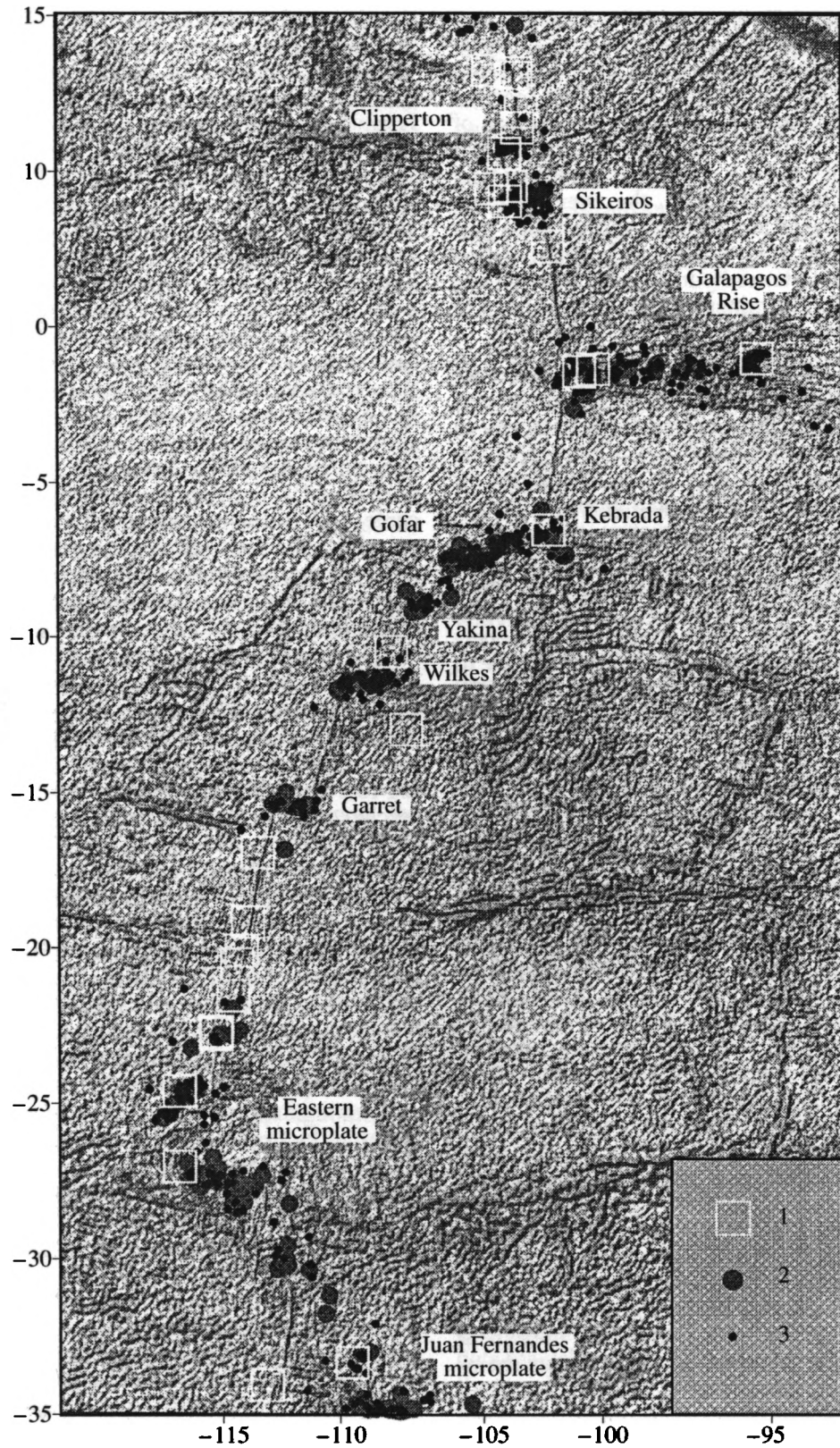


Fig. 1. (Contd.)

first generalizing works on the seismicity of MOR belongs to Sykes (1972), who noted its following characteristic features: planetary scale, distinct localization of epicenters along the ridge axis, absence of intermediate and deep-focus earthquakes, and reflection of tensile tectonics in seismicity. Evidently all these features of MOR seismicity are caused by the very nature of these structures. It should be noted that, despite the fact that the ridges themselves are geomorphologically wide structures (up to 3000 km), the overwhelming majority of earthquakes are concentrated within a narrow zone of a few tens of kilometers wide, the so-called extrusive zone. The intense hydrothermal activity and associated metalliferous mineralization are confined to the same zone.

When passing to the next level, any sufficiently large part of the ridge is divided into rift areas (spreading centers) connecting them to transform fractures. In recent works (Sobolev and Rundqvist, 1996, 1998), the authors tried to generalize data on the seismicity of transform and rift areas of MOR on a global scale and to determine the role of both structure types in the MOR seismicity. Conclusions about the decisive role of transform fractures in the seismicity of MOR, made previously for separate sites (Francis, 1968; Drumya *et al.*, 1990; Boldyrev, 1994), were confirmed. The energetic contribution of transform fractures exceeds one to two orders of magnitude that of rift parts of the MOR, and this relationship grows with the spreading rate increase.

Therefore, at the given level, the distribution of seismic activity becomes inhomogeneous, and the strongest events are confined to zones with an increased thickness in the lithosphere, i.e., to active areas of transform fractures with a predominant shear environment. On the contrary, almost all known fields of the modern hydrothermal activity and associated ore occurrences are within the boundaries of rift areas of MOR, where the lithosphere is thinnest, and tension takes place. Hydrothermal oxide and silicate crusts, as well as the dissemination of sulfides, were detected in a number of transform fractures of the Mid-Atlantic Ridge (Rona, 1986). However, it remains obscure whether this mineralization was formed within the boundaries of transform fracture or whether it appeared on the adjoining linear segments of spreading and subsequently was simply exposed in the escarpment of a transform fracture. It is also evident that the relation of most metalliferous depressions in the Red Sea with transform fractures is only indirect. The parallelism between the long axes of depressions and the axis of spreading indicates that these depressions are located along rift areas near transform fractures rather than on the fractures themselves (Rona, 1986). Therefore, at the given level of MOR segmentation, the negative correlation between seismicity and mineralization is observed.

The transition to the next segmentation level is connected with the division of linear rift areas of MOR into

segments with the dimensions averaging on the order of 100 km. Owing to bathymetric surveys, as well as to detailed works, with the help of multibeam echo sounders and lateral-vision sonar systems, a complicated hierarchic structure of spreading centers has been revealed (Macdonald *et al.*, 1988; Dubinin *et al.*, 1990). It has turned out that a longitudinal zonality of several orders exists, which may be interpreted as a manifestation of independent spreading cells (Francheteu and Ballard, 1983). The central part of each segment is usually elevated with respect to the margins; this is supposed to be connected with a different magma supply. The zones that are interpreted as magmatic chambers were detected under many segments of fast-spreading ridges, and this has become one of the most important discoveries of recent decades. However, according to seismic tomography data, these chambers do not look like a continuous zone, but sooner resemble narrow discontinuous lenses (Solomon and Toomey, 1992). Under slow-spreading ridges, magmatic chambers have not been found. It has been suggested that two phases (volcanic and tectonic) alternate in time here. Discrete eruptions of basalt occur during the first phase, while the ridge destruction and formation of fissures and vertical faults take place during the second phase against a background of continuing tension.

The longitudinal zonality inside the segments is mirrored in the distribution of earthquake hypocenters. In accordance with existing models of segmentation, lithosphere margins must be thicker than the central part; hence, tectonic processes of tension play the leading role here. One may expect that fracture formation reaches large depths and seismicity is higher in these areas. These considerations have been supported by observations. Huang and Solomon (1988) demonstrated that on slow-spreading ridges, the largest earthquakes are confined to edges of the segments. This is clearly seen from the distribution of hypocenters in the central parts of MAR and EPR (Figs. 1a, 1b). The focal depth of earthquakes systematically grows with the increase of spreading rate, which also mirrors the relation of earthquake intensities with the thickness of the elastic layer in the lithosphere.

Although we may as of yet only suppose the distribution of hydrothermal fields within the boundaries of rift areas of the MOR, the same tendency of their localization in the marginal parts of segments, near the intersections of spreading centers with transform fractures or nontransform displacements, can be followed for the MAR (Fig. 1a). This regularity is less pronounced for the EPR (Fig. 1b). This can be explained in the following way. In contrast to ridges with a high spreading rate, for which the axial magmatic chamber is typical, anomalous thermal or tectonic conditions are required for the appearance of a crustal source at low spreading rates (*Gidrotermal'nye ...*, 1992; Poroshina and Krasnow, 1996). It is evident that the coincidence of zones with active magma generation and weakened areas in the crust is necessary for the appearance of stable high-

temperature hydrothermal circulation. Two types of ore-controlling situations—"central" and "marginal"—may be distinguished on the basis of analysis for known hydrothermal fields. In the first case, ore occurrences are confined to apical grabens of axial extrusive ridges; in the second case, they are located along marginal fractures of the rift valley. Transverse tectonic disturbances—nontransform displacements and intrasegmental dislocations—play the most important role in either case. These disturbances basically differ from transform fractures and manifest themselves as zones where a displacement or change of the strike of basic structural elements take place. They are responsible for the division of rift areas of the ridge into segments of higher orders. All ore occurrences of the MAR are located at intersections of axial and transverse dislocations or immediately near them, which is less typical for the EPR. Here, hydrothermal ore formation is chiefly governed by magmatic processes (Poroshina and Krasnov, 1996). Nevertheless, the direct correlation between seismicity and hydrothermal activity, at the given hierarchic level, is confirmed for both of the areas on distribution graphs for the total seismic moment along the ridge (Figs. 2a, 2b). One can distinctly observe the seismic activity increase around the intersections of spreading centers with transform fractures at a sufficiently large averaging interval (1° in latitude), as well as the tendency toward localization of hydrothermal fields at the same sites. However, if the interval of averaging is decreased by one order of magnitude, big maximums, as a rule, break into several small ones that do not spatially coincide with sulfides of ore occurrences. This allows us to suggest the inverse character of correlation at the next, most detailed level of segmentation. However, here we have to base our research on the results of separate detailed experiments for a number of MOR areas.

Special investigations of axial valleys using bottom seismographs and hydrophones were carried out in the rift area of the MAR in the 23°N region situated within the southern end of the ridge segment. Source parameters were determined for many earthquakes (Toomey *et al.*, 1985). Microearthquakes were mainly recorded under the bottom of the axial valley at depths of 5–8 km. They belong to normal faults, with the dip angle not less than 30° . This indicates that the tension-related brittle fracture formation in the lithosphere under the ridge was extended up to the specified depths, and magmatic processes were not related to seismicity. The results of seismic prospecting are also indicative of the normal crust structure.

Different results were obtained in other areas of the MAR that are characterized by increased hydrothermal activity. The first of them is located in the 26°N region in the central part of the segment and includes the active hydrothermal field TAG (Kong *et al.*, 1992). A zone of reduced spreading rates was detected under the along-axis high at a depth of 4–8 km. This zone is interpreted as a region of recent magma intrusion, which, though

solidified, still retains a high temperature. The absence of earthquake centers is in agreement with this fact. Mechanisms of earthquakes are much more diversified here and point to different orientations of stresses. It is important to note that, of 189 events, not a single one was recorded directly under the high-temperature hydrothermal field. The epicenters are located westward and eastward of the TAG (Fig. 3). Evidently, the absence of microearthquakes near active hydrothermal fields may be attributed to anomalously high temperature gradients in these areas, which is a necessary condition for the formation of ore occurrences (Rona, 1986).

The second area is situated in the 29°N region and includes the Broken Spur hydrothermal field (Wolfe *et al.*, 1995). Here, microearthquakes are located predominantly within two zones. The greatest activity was observed within the interior angle of nontransform displacement. The solutions of focal mechanisms indicate that faults prevail here; these events are apparently connected with tensile processes. On the contrary, the analysis of mechanisms suggests that events in the central part of the segment (and also near the hydrothermal field) are connected with the processes of volcanism and hydrothermal activity.

Somewhat different specific features were revealed during the study of microearthquakes within the boundaries of fast-spreading ridges of the Pacific Ocean. Their low seismic activity and small depths of hypocenters (less than 3 km) were noted long ago. It has been supposed that, in this case, the seismicity more strongly reflects magmatic and hydrothermal processes intensely proceeding on the ridges. Thus, no earthquakes were observed on the Cleft segment (Juan de Fuca Ridge) using teleseismic and hydroacoustic methods, and a great number of earthquakes with a very small magnitude was revealed only after the installation of bottom seismometers (Hildebrand *et al.*, 1997). However, the hypocenter position could not have been determined for the majority of them. The coincidence (in plan) of these events with the hydrothermal "megaplume" zone (Sohn *et al.*, 1995), as well as the similarity of their characteristics with those of events occurring near volcanoes and geysers (for example, the grouping of earthquakes in swarms), gives grounds to suppose that in this case, a source of many microearthquakes is connected with the hydrothermal activity within boundaries of the MOR; however further investigations are needed to verify this hypothesis.

Therefore, the joint consideration of seismicity and hydrothermal mineralization of MOR, on the basis of data available to date, makes it possible to arrive upon the conclusion that it is necessary to distinguish several hierarchic levels or scales of investigation, bearing in mind that, depending on the scale, the character of these relations can be reversed. Previously, analogous interrelations were noted for other natural formations (Rundqvist, 1971). An attempt to generalize the results

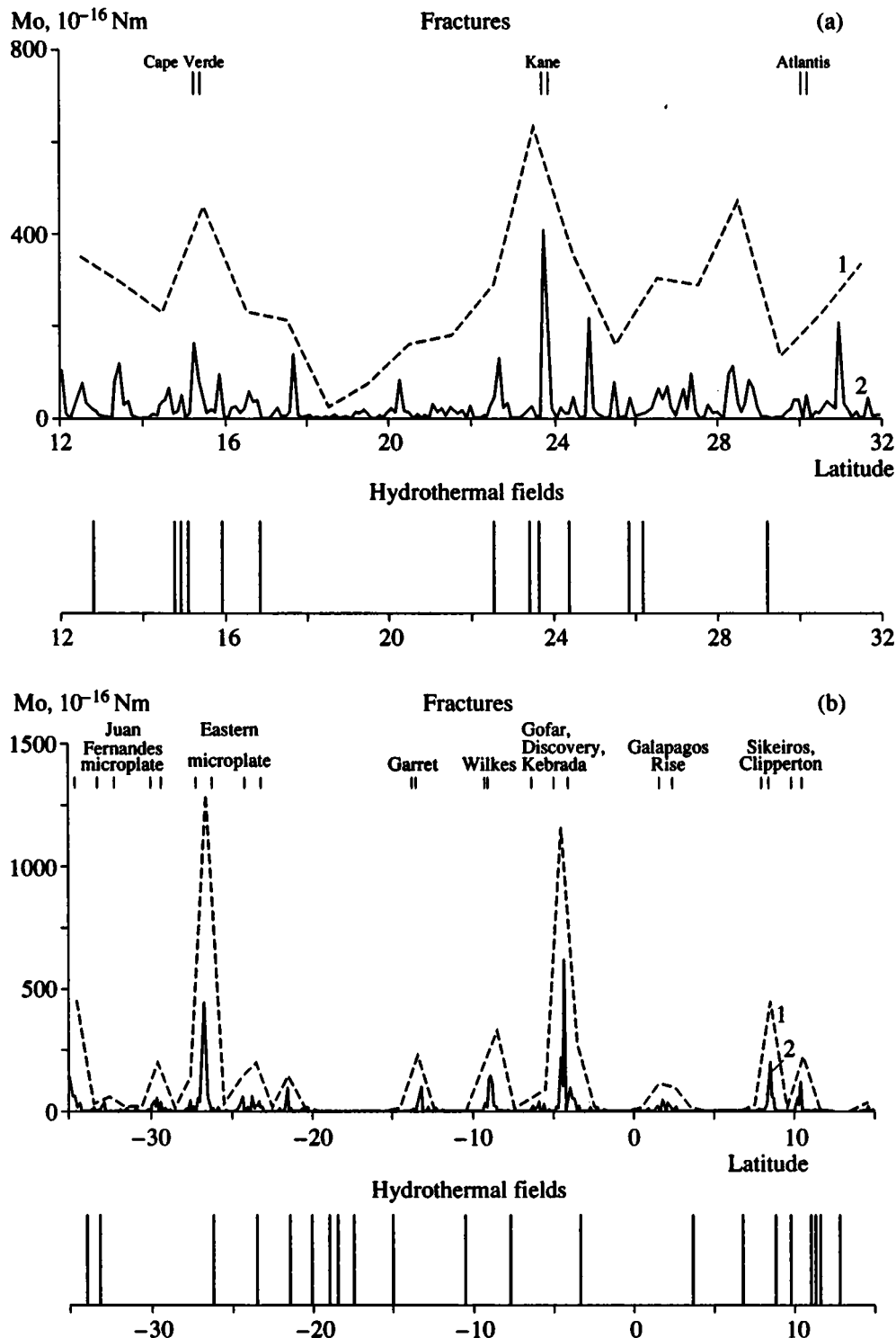


Fig. 2. Distribution of the total seismic moment in latitude for (a) the Mid-Atlantic Ridge and (b) the East-Pacific Rise. The locations of hydrothermal fields and transform fractures are also shown. (1) Interval of averaging in latitude 1° ; (2) interval of averaging in latitude 0.1° .

of investigations was made in our work (table). As with many investigators (Macdonald *et al.*, 1988; Dubinin *et al.*, 1990), we conditionally distinguish five levels of MOR segmentation structures. The whole ridges,

whose boundaries are most frequently represented by triple conjugations of plates, belong to the first order segments. The second order segmentation is pronounced most clearly and consists in the division of

Relationships between seismicity and hydrothermal mineralization depending on the MOR segmentation level

Segmentation level		Average dimensions, km	Boundary structures	Character of correlation between seismicity and mineralization
1	MOR as a whole	>1000	Triple conjugations	Direct
2	Rift areas (spreading centers)	100–1000	Transform fractures	Inverse
3	Segments within rift areas	20–100	Nontransform displacements	Direct
4	Local tectonic structures	20–1	Intrasegmental displacements	Inverse
5	Hydrothermal fields	<1	–	Direct

MOR into rift areas (spreading centers) and transform fractures. At this level, the correlation of seismicity and hydrothermal mineralization is solely of an indirect character, and its sign is quite obvious. Furthermore, rift areas are separated by nontransform displacements into smaller parts a few tens of kilometers in size. The results of preliminary analysis for the EPR, and especially for the MAR, show that at the given level there more likely exists a direct correlation between the distribution of hydrothermal fields and the areas of earthquake manifestation owing to the coincidence of tectonically weakened and seismic zones. Subsequent analysis is restricted to several sites, where detailed investigations of microearthquakes were carried out by means of local temporary networks using either acoustic buoys or bottom seismometers. The localities of increased seismicity and active ore formation within fourth order segments do not coincide, most likely due to the influence of thermal field inhomogeneities. Finally, based on a few works, it is possible to suggest

the volcanogenic and even hydrothermal nature of some low-magnitude events within the hydrothermal field boundaries. Naturally, this series can be continued further, up to tectonic fractures with dimensions on the order of tens of meters, and such investigations have already begun (Wright, 1998). However, the data remain obviously insufficient.

It is clear that as of yet we can speak only about the correlation sign between seismicity and hydrothermal activity, rather than about its quantitative aspect. The intensity of earthquakes rapidly diminishes with the decrease of seismogenic structure dimensions in accordance with the known empirical dependence $M_s \sim \log L^3$, where L is the fracture length (Kanamori and Andersen, 1975). In fact, as we previously mentioned, the magnitude of strongest earthquakes diminishes from 6.0 to 2.0 during the transition from the scale of MOR, as a whole, to local tectonic disturbances. In this case, without any doubt, only an insignificant portion of deformations is reflected in the seismicity. Assessments accomplished for large segments of MOR indicate that the major part of deformation energy is associated with the aseismic deformation: only 1 to 10% of energy is released during earthquakes. It should be also kept in mind that this relationship diminishes with the decrease of the spreading rate (Sobolev and Rundqvist, 1998).

CONCLUSION

Despite restrictions due to inadequate study, the joint consideration of spatial relations between the seismicity and hydrothermal mineralization of MOR allows us to conclude that it is necessary to distinguish several hierarchic levels or scales of investigation. Depending on the scale, the character of these relations can be reversed. Five levels of MOR segmentation structures can be conditionally distinguished. The whole ridges, whose boundaries are most frequently represented by triple conjugations of plates (the coincidence of seismicity and mineralization zones, i.e., the direct correlation), belong to segments of the first order. The segmentation of the second order is the most distinctly pronounced and consists in the division of MOR into rift areas (spreading centers) and transform fractures. The seismicity of transform fractures is higher, on average, by one order of magnitude (inverse correla-

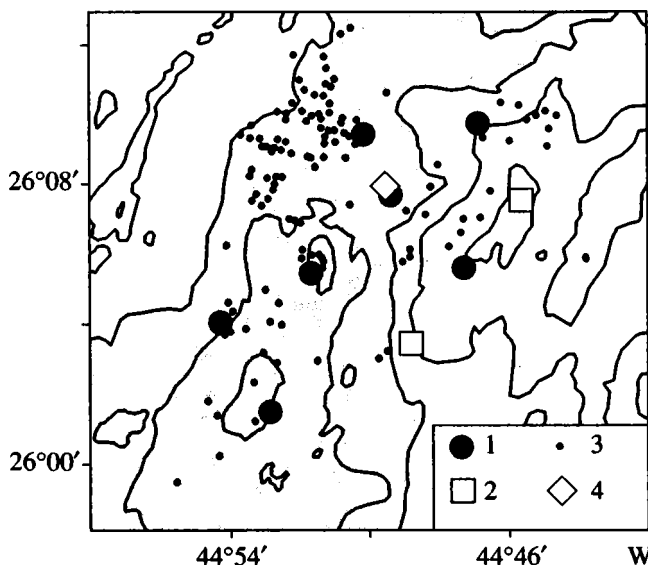


Fig. 3. Microearthquakes in the Mid-Atlantic Ridge sector near 26°N. Isolines of depth are shown at intervals of 0.5 km; the dark sector lies below 3.5 km. (1) Locations of hydrophones; (2) locations of bottom seismometers; (3) epicenters of microearthquakes; (4) TAG hydrothermal field.

tion). The rift areas are separated by nontransform displacements into smaller parts that are several tens of kilometers in size. The results of preliminary analysis for the EPR, and especially for the MAR, show that, at the given level, there more likely exists the direct correlation in the distribution of hydrothermal fields and earthquakes owing to the coincidence of tectonically weakened and seismic zones. Further analysis is restricted to several sites of detailed works on the study of microearthquakes by means of local temporary networks. The locations of increased seismicity and active hydrothermal ore formation within the segments of the fourth order do not coincide, and this seems to be connected with the influence of thermal field inhomogeneities. Finally, based on a few works, it is possible to suggest the volcanogenic and even hydrothermal nature of some microearthquakes within the hydrothermal field boundaries.

Of course these conclusions are of preliminary character and, no doubt, will be refined in the future. Nevertheless, these regularities may prove useful in the course of subsequent complex investigations of MOR.

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SHORT COMMUNICATIONS

Problems of Phosphatic Raw Material in Russia (All-Russian Symposium)

The All-Russian Symposium "Problems of Phosphatic Raw Material in Russia" was held on September 15–17, 1998, at the Meleuz Mineral Fertilizers Plant, Joint-Stock Company (OAO) Minudobreniya, Meleuz, Bashkortostan.

The objectives of the symposium were to determine ways of providing Russia and, in particular, Bashkortostan with phosphatic raw material and to discuss geological and genetic problems of phosphorite formation as the scientific background for expanding the phosphatic raw material base.

Organizers of the symposium included (1) Section of Phosphorite-Bearing Formations of the Lithological Committee, Russian Academy of Sciences; (2) Bashkortostan State Committee on Geology and Utilization of Underground Resources; (3) Ministry of Agriculture and Food of Bashkortostan; (4) Minudobreniya, Meleuz; and (5) State Research Institute of Mining and Chemical Raw Material (GIGKhS).

The symposium represented a traditional scientific workshop on the geology of phosphorites, which was regularly held once every 3–5 years by the Section of Phosphorite-Bearing Formations. It was attended by many geologists and interdisciplinary specialists who dealt with phosphorites. It was the eighth symposium during the past 30 years.

Those participating in the symposium were 63 representatives from 27 institutions, including those from 12 research and educational institutes. The symposium was preceded by a publication of abstracts by 34 announced papers. Twenty-one oral presentations were made, and 18 specialists participated in the discussion. During the symposium, excursions to the Seleuk phosphorite deposit, the Meleuz mineral fertilizers plant, as well as Permian and Carboniferous deposits in the Nugush reservoir area, were organized for the participants. The government, several ministries and committees of Bashkortostan, and local official bodies attached much importance to the symposium and offered exclusively good conditions for its operation.

The symposium was opened by M.A. Shakirov, Chairman of the Organizing Committee, and Deputy Prime Minister of Bashkortostan. I.A. Al'mukhametov, the General Director of Minudobreniya, greeted the symposium. The opening address was presented by A.S. Sokolov, Chairman of the Section of Phosphorite-Bearing Formations, and Cochairman of the Organizing Committee. The sessions proceeded in 3 sections:

(1) prospects for the development and exploitation of the phosphatic raw material base in Russia and abroad: mining–technological, economic, and environmental problems; (2) geological and genetic problems; and (3) the phosphatic raw material base of Bashkortostan: prospects of its development and exploitation.

The symposium was aimed, first of all, at solving the problems of improving the phosphatic raw material base in Russia. Its state and prospects of development were elucidated and analyzed by A.I. Timchenko, Director of GIGKhS, who said in his speech that the large-scale production of P-bearing fertilizers will soon run into a shortage of phosphatic raw material. Among 850 Mt of recognized P_2O_5 reserves suitable for development, only 337 Mt are ready for mining. He also formulated principal tasks for improving and augmenting the phosphatic raw material base.

The situation and geological prospects of developing the phosphatic raw material base of Russia were considered in the paper by R.M. Faizullin, Central Research Institute of Geology of Nonmetallic Minerals (TsNIIgeolnerud). He emphasized the leading position of Russia in reserves and potential resources of apatite, which represented the main raw material for production of phosphorus-bearing fertilizers in the country. Cessation of exploitation of the Egor'evsk and Polpino deposits, as well as the reduction of mining at the Vyatka–Kama deposit, caused a sharp decrease in the phosphorite flour production and provoked the necessity of creating new raw material bases, the prospects for which are available. The geological prospecting and especially prognostic and mineragenic studies of phosphates have drastically dropped. The paper by V.P. Perova, Senior Researcher of GIGKhS, was devoted to prospects of considerable increase in the recovery of phosphorite mining at the Vyatka–Kama deposit, the largest in Russia, along with an expansion of its use for the production of not only phosphorite flour, but soluble fertilizers and yellow phosphorus as well.

Yu.A. Kiperman *et al.* from the All-Russian Institute of Mineral Resource Economics (VIEMS) elucidated the situation with the world demand and consumption of mineral fertilizers exceeding 130 Mt of nutrients annually. At the inception of the 21st century, the annual demand for mineral fertilizers and phosphorus-bearing fertilizers is expected to rise by 2.5% and 2.8%, respectively. The main consumers of fertilizers are countries of Southeast Asia, especially China and India. Large-scale mining of phosphorites and the pro-

duction of phosphatic fertilizers is planned in the near future for Australia, Saudi Arabia, and Peru. Particular attention in the report was given to the environmental impact from phosphate mining and processing in the USA, as well as to measures used to prevent detrimental effects.

Phosphate raw material is the basis for producing the phosphorus-bearing fertilizers extremely necessary for P-depleted fields in Russia. P.V. Klassen, Director of the Research Institute of Fertilizers and Pesticides (OAO NIUIF), lectured on the situation and prospects of developing the production of phosphorus-bearing fertilizers in Russia. In 1997, the output amounted to only 36% of production capacities available, but the main part of the products were exported, and the domestic consumption made up only 20%; the use of nutrients for plants fell to the level during the 1960s (10–12 kg/ha). The report suggested concrete organizational, economic, and technological measures, which might increase the supply of fertilizers to agriculture by a factor of ten during 5–6 years.

The expected rise in the deficiency of phosphatic raw material in Russia requires the urgent mobilization of phosphoritic ores for production of soluble fertilizers, which have not been previously used for this purpose in Russia. Several reports were devoted to the solution of the problem. A.I. Angelov *et al.* (NIUIF) reported the technology elaborated by his group for a partial substitution of apatite concentrate for phosphorites to obtain calcium dimonophosphate. The agricultural efficiency of this technology was comparable with that of double superphosphate, while the net cost of P_2O_5 material decreased by 33%. The problem of utilizing phosphoritic raw material in production of compound fertilizers was elucidated in reports of V.G. Kazak *et al.* (NIUIF) and A.G. Balabushevich *et al.* (GIGKhS). A.A. Krasnov (Agroeko) discussed the problem of establishing minor enterprises for producing phosphorite flour and organomineral fertilizers.

A pioneer in mechanochemical technology for processing phosphoritic ores was reported by researchers of the Institute of Solid Fuel Chemistry and Mineral Resources (IKhTTiMC), Siberian Division, RAS (Novosibirsk). The vibratory centrifugal mill devised in this institute provided an experimental–industrial processing of Mongolian phosphorites without any waste waters or environmental pollution.

The presentation by A.F. Georgievskii (the Russian University of People's Friendship) attracted particular interest. It was devoted to the biogeotechnological method for concentrating phosphate ores. The method was elaborated at GIGKhS and Agroeko in cooperation with the Institute of Microbiology, Biochemistry, and Physiology of Microorganisms, RAS. It is based on the recovery of mineral components by the effect of microorganisms or their metabolites. The application of the method for phosphatic raw material is unknown in world practices. By using culture liquids for low-grade

ores, one attains a high phosphate leaching rate that considerably exceeds the capabilities of nitric- and sulfuric acid decomposition. Much attention was concentrated on the use of the method for phosphate–carbonate ores that are resisted to concentration by traditional methods. The recovery of dolomite and calcite from the ore was as high as 90–95% and 100%, respectively. The method is especially effective if the phosphate matrix is covered with carbonate dissemination that is typical of phosphorite ores from many deposits, the Seleuk one included.

The paper presented in the Section of Geological and Genetic Problems by E.L. Shkol'nikov *et al.* (Institute of Geology, Far East Division, RAS) attracted considerable interest. It was devoted to the results of ultramicroscopic studies of Seleuk phosphorites, which were carried out for the first time. Similar studies of phosphorites in many countries revealed an abundance of phosphatized fossils, microbiota included. The relation of phosphorites to organogenic material is observed in phosphorites of the Seleuk deposit as well. A similar problem on the role of bios in phosphorite formation was discussed in the paper by A.S. Sokolov (GIGKhS), who showed the undeniable importance of fossils in activation of the phosphate recovery from bottom waters, which represent undersaturated solutions, by substituting skeletons and soft tissues. The process is governed by the laws of geochemical interactions. A share of biogenic phosphorus in phosphorites is negligible.

G.M. Sedaeva (Moscow State University) elucidated conditions of the formation of marine phosphorites, based on Upper Jurassic deposits in the eastern part of the East European Platform. Repeated transgressions caused the drift of a great amount of biophile nutrients to sedimentation basins that enhanced the biota bloom. Organic matter accumulated in the sea floor depressions. The primary concentration of phosphate and subsequent formation of its interlayers occurred due to the decay of the organic matter.

The problem of improving soil fertility in Bashkortostan and utilizing of local phosphate and other agricultural raw materials for this purpose was the particular concern at the symposium. Shakirov, Vice Prime Minister, devoted part of his speech to this problem. The Meleuz plant of mineral fertilizers is short of phosphatic raw material; so the search for local sources is one of the principal tasks of the geological service in the republic. A detailed substantiation of the need for improving soil fertility in Bashkortostan by utilization of local agricultural raw material, was presented by A.M. Galiev, Vice Minister of Agriculture and Food.

The oral presentation of R.A. Khamitov, Chairman of the State Geological Committee (SGC) of Bashkortostan, was devoted to prospects and ways of mobilizing local phosphates. He characterized in detail the local phosphorite deposits, such as Seleuk, Ashin, Sima, and Kukashkin, with the total reserves exceeding

10 Mt. The last deposits named are ready for developing. At the Seleuk deposit, an experimental quarry should be laid simultaneously with exploration work. The SGC of Bashkortostan has elaborated the problem of revealing new deposits in accordance with the Concept of the State Policy of the Bashkortostan Republic in the Field of Utilization of Natural Resources. M.G. Gil'mutdinov, Director of the State Station of the Agrochemical Service, analyzed in detail the problem of phosphorus in agriculture of Bashkortostan and emphasized that the demand in phosphorite flour might reach about 2.5 Mt in the near future.

Agroefficiency of phosphorite flour on fields in Bashkortostan was elucidated in the report delivered by N.A. Sereda (Institute of Agriculture of Bashkortostan). The same questions were raised and emphasized during the discussion of the problem.

Primary tasks of preparation for the development of the Seleuk deposit were considered in the paper by A.S. Sokolov and A.A. Krasnov. G.Sh. Zhdanov reported on the geological, mining, and technological characteristics of the deposit when participants of the symposium visited it.

The way the symposium was organized and held received unanimous recognition among the participants. Presently, such communications between scientists and specialists in phosphate geology are certain to be very important and necessary. At the closing session, a resolution was adopted which comprised recommendations on the three above-mentioned sections of the symposium.

According to recommendations on the improvement of the phosphatic raw material base of Bashkortostan, top priority should be given to the predevelopment stage preparation of the Seleuk deposit and the search for new phosphorite deposits. In this connection it is pertinent to elucidate briefly the prospects of the phosphorite potential in Bashkortostan and the problems of developing the Seleuk deposit.

The analysis of materials on the phosphorite potential in Bashkortostan, which have been gathered for over 60 years, shows that the Bashkortostan territory, which represents a part of the cis-Urals phosphorite-bearing basin, is composed of two submeridional zones

of Permian phosphorite-bearing formations (Asselian-Sakmarian and Artinskian). The Seleuk deposit is confined to the Asselian-Sakmarian formation in the south, whereas the Khashinov, Arlanov and some other phosphorite occurrence are located in the north. The Artinskian formation is characterized by phosphorite occurrences in the south near Sterlitamak. The northern area incorporates a series of occurrences, among which the Abdullin occurrence is situated at the northeastern boundary of Bashkortostan. Geological prospecting can reveal new phosphorite deposits within these zones.

The exploration work at the Seleuk deposit should be resumed without delay. The negative assessment of its commercial value, made in the past, was caused by unsuccessful processing of specific phosphate-dolomite ores. The attempt was doomed to failure for the lack of a selection method for these mineral components at that time. By now the problem has been solved by the experience of concentrating similar ores at the Kingisepp, Karatau, and other deposits, and effective methods for concentration of such ores have been elaborated.

In the 1990s, on the assignment of Bashgeologiya, GIGKhS suggested new schemes for the treatment of Seleuk ores and the separation of high-quality ore concentrates, which could serve as an additional source of phosphate raw material for the Meleuz plant. The reassessment of the Seleuk deposit showed that a third of its reserves could be developed by strip mining with low investments and simplest technical facilities, and adjacent areas were promising for augmenting the reserves.

Objects of top-priority for the Seleuk deposit are: (1) selection of representative technological samples; (2) approbation of the suggested concentration schemes to them; (3) selection and substantiation of the most efficient schemes. An energetic realization of recommendations suggested will allow augmenting and mobilizing the local phosphate resources to cover the needs of Bashkortostan.

A.S. Sokolov, State Institute of Mineral and Chemical Resources
and **A.A. Krasnov**, Agroeko

SHORT COMMUNICATIONS

World Oil Resources in the 21st Century

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Abstract—Prognostic oil resources are calculated for sedimentary rocks of petroliferous basins of the world on the genetic basis. The volume of clayey rocks considered as potential oil source rocks (40%) in basins and their share (2/3 part of potential oil source rocks) in the main oil-generating zone were taken into consideration. The average amount of liquid hydrocarbons is equal to 930 g/m^3 in oil source rocks of the main zone with organic matter content of 0.5–3.0%. Average values of the emigration and accumulation coefficients of oil (0.4 and 0.2%, respectively), oil consumption for the formation of natural bitumens, oil loss during migration, oil pool destruction, etc. were used in the calculations. The potential oil resources estimated on the genetic basis are $420\text{--}510 \times 10^9 \text{ t}$.

The prediction of world oil resources determines not only the energy potential of separate regions, but also their strategic importance. Estimations of potential oil resources became especially pressing in the 20th century and, therefore, have been carried out repeatedly. In doing so, as a rule, the later estimates were found to be many times higher than the previous ones and always were confirmed by discoveries of new hydrocarbon (HC) fields of oil and condensate gas. For example, early in the 20th century, L. Wicks evaluated the world oil reserves at $9.5 \times 10^9 \text{ t}$, but already by 1958, they had grown up to $207 \times 10^9 \text{ t}$, and at the end of the century the reserves are estimated at $540 \times 10^9 \text{ t}$. Such differences in the estimations of the world oil resources can be explained by the advancement in methods of prospecting for HC, the progress in theoretical investigations in the field of oil and gas genesis, the use of geophysical and geochemical studies, and the genetic approach to the evaluation of oil and gas potential. Such an approach enhances the efficiency and reliability of prospecting for petroleum and allows for more reliable planning of oil extracting and refining industries. There are different techniques for the estimation of potential oil resources in sedimentary rocks. The most traditional techniques embrace the “structural-reference” and “balance” methods. According to the structural-reference method, the revealed oil resources in already known structures are quantitatively comparable with HC reserves in as yet undetermined structures of an oil- and gas-bearing basin (OGB). The balance approach is based on the comparison of the proven volumes of HC with the calculated potential reserves contained in similar geological structures.

In the second half of the 20th century, as a result of a progress achieved in the field of oil genesis, a new genetic approach to the evaluation of oil reserves in sedimentary basins was developed. This method is based on the main principles of the sedimentary-migration theory of oil genesis (Vassoevich, 1967), the well-

known regularities of the transformation of dispersed organic matter (DOM) during lithogenesis, the quantitative assessment of HC produced in the main oil-generating zone (MOZ), and the scales of HC emigration and accumulation in natural reservoirs.

At the end of the 1970s, Vassoevich noted that the problem of oil origin is principally resolved, and further works must be aimed at the development of methods of quantitative assessment of HC produced in oil source rocks at different stages of sedimentary rock evolution rather than at the study of qualitative characteristics of oil. In the 1980s–1990s, with the introduction of new instrumental methods for the analysis of dispersed OM, it became possible to determine the oil potential of OM (pyrolysis method), the specific productivity of rocks (t/km^3) and sedimentary units (t/km^2), etc., i.e., to turn to the quantitative evaluation of potential oil resources in OGB on the genetic basis. Some formulas were proposed allowing for the estimation of productivity of rocks, sedimentary units, and an entire basin with the help of minimum analytical information about the studied object (Korchagina and Chetverikova, 1983; Korchagina, 1986).

During the current study, the evaluation of potential resources of liquid HC (oil) was carried out for sedimentary rocks in oil- and gas-bearing basins of the world. In our computations, the volume of OGB rocks is taken as $330 \times 10^6 \text{ km}^3$ ($308 \times 10^6 \text{ km}^3$, according to Kalinko, 1964). Of the total volume of sedimentary rocks, clayey rocks, which make up about 40% ($130 \times 10^6 \text{ km}^3$) of OGB sedimentary rocks, were chosen as potential oil source formations. According to Ronov (1990), clays account for 51% of the Earth's sedimentary cover. This assumption is quite compatible with our calculations. Of the total volume ($130 \times 10^6 \text{ km}^3$) of clayey (potential oil source) rocks in OGB, about 2/3 (i.e., $87 \times 10^6 \text{ km}^3$) is situated inside the main oil-generating zone, and the remaining 1/3 is located either

above or below the MOZ, or is already completely exhausted. Therefore, the volume of potential oil source rocks in OGB equal to $87 \times 10^6 \text{ km}^3$ was accepted for the computation of HC generated in rocks in the mesocatagenetic (MK) zone (the main oil-generating zone is located at stages MK_1 to MK_3 of mesocatagenesis). As is well known, oil source rocks are differently enriched in organic matter (from 0.1 to 10%). The most typical OM content (0.5–3%) in clayey oil source rocks was chosen for the computations. We calculated the quantity of HC generated under conditions of mesocatagenesis (MK_1 – MK_3) in rocks with such DOM concentrations. The HC generation under such conditions is governed not only by the concentration of dispersed OM in rocks, but also by its initial composition. Our calculations were based on the assumption that organic matter of intermediate composition (type II, according to foreign scientists, and sapropelic, according to Russian scientists) participates in the HC generation in oil source units. Average specific HC contents (75, 150, and 440 g/m^3) were accepted as background initial HC concentrations in oil source rocks above the main oil-generating zone. The average specific HC content was 220 g/m^3 for all rocks at the mesocatagenetic stage. The quantity of HC generated at each stage of catagenesis was computed, and the average specific content of liquid HC was determined (930 g/m^3) for rocks with different concentrations of dispersed OM. For clayey oil source rocks in the MOZ ($87 \times 10^6 \text{ km}^3$), the average amount of liquid HC was equal to: $87 \times 10^6 \text{ km}^3 \times 930 \times 10^3 \text{ t/km}^3 = 81 \times 10^{12} \text{ t}$. Only part of liquid HC emigrates from oil source rocks, depending on the structure of the sedimentary sequence. In this case, the value 0.4 can be adopted as the average coefficient of emigration. A quantity of HC emigrating from oil source rocks is $32 \times 10^{12} \text{ t}$. Up to 10% of liquid HC can dissolve in stratal water. In our calculations, the liquid HC amounts to $3.2 \times 10^{12} \text{ t}$. A significant part of liquid HC is lost in the process of migration, and its possible accumulation in pools may amount to about 20% of the initially emigrated HC, i.e., $5.8 \times 10^{12} \text{ t}$ (without HC dissolved in water).

Based on the world's proven reserves of bitumens (ca. $960 \times 10^9 \text{ t}$), it is assumed that not less than $3 \times 10^{12} \text{ t}$ of oil were expended in their formation. In such a case, $2.8 \times 10^{12} \text{ t}$ of oil had to be remained in oil pools. The complex geological evolution of OGB repeatedly led to the destruction of oil pools, and the losses may run as high as 40–50% of the initial reserves. In this case, geological resources of oil can be estimated at $(1.4\text{--}1.7) \times 10^{12} \text{ t}$, and the initial extractable reserves of oil (together with liquid HC from condensate) are estimated at $(420\text{--}510) \times 10^9 \text{ t}$. A.E. Kontorovich and V.I. Demin evaluated the initial extractable oil reserves at $660 \times 10^9 \text{ t}$. M.S. Modelevskii assumed $(330\text{--}400) \times 10^9 \text{ t}$ (geological resources at $1.5\text{--}2.0 \times 10^{12} \text{ t}$). V.I. Vysotskii estimated initial extractable oil reserves at $540 \times 10^9 \text{ t}$. As seen from the above cited figures, initial extractable oil reserves (with a broad range of val-

ues, from 330 to $660 \times 10^9 \text{ t}$), according to different authors, are close to $400 \times 10^9 \text{ t}$. According to our calculations, they vary from 420 to $510 \times 10^9 \text{ t}$. According to Hunt (1982), sedimentary rocks contain $54 \times 10^{14} \text{ t}$ of organic carbon, and only 2% of this quantity ($110 \times 10^{12} \text{ t}$) is transformed into micro-oil. Of this quantity of micro-oil, oil proper accounts for 0.5%, i.e., $5.5 \times 10^{12} \text{ t}$ ($5.8 \times 10^{12} \text{ t}$ from our computations). This value comprises also oil expended in the bitumen formation and other losses.

It is of interest to compare the total quantity of dispersed forms of liquid HC in clayey rocks with the possible quantity of oil in pools. According to Vassoevich *et al.* (1973), in the continental sector of the stratosphere, clays account for 51.4% (51.1%, according to Ronov, 1990) of the entire sedimentary cover, i.e., $60 \times 10^{16} \text{ t}$. This volume of clay contains $120 \times 10^{12} \text{ t}$ of liquid HC in dispersed form ($144 \times 10^{12} \text{ t}$, according to Kalinko, 1964). From our calculations, $5.8 \times 10^{12} \text{ t}$ of oil should accumulate, which amounts to 5% of the total quantity of dispersed liquid HC in rocks ($120 \times 10^{12} \text{ t}$).

Ronov (1993) studied the intensity of DOM and oil accumulation in Cambrian–Neogene sedimentary rocks and established a clear correlation between them. He came to the conclusion that the largest industrial oil pools were formed under conditions of high OM content in sedimentary rocks, and in this case the bulk of oil is genetically related to organic matter of oil source rocks. Calculations made by Ronov (1993) show that the total mass of organic carbon, situated in the Earth's sedimentary cover from the Late Jurassic to the Pliocene, is $509 \times 10^{13} \text{ t}$, and the world oil resources (perhaps "proven reserves" are meant) in these deposits are $124 \times 10^9 \text{ t}$. According to our calculations, the world geological potential reserves of oil, together with liquid HC in condensate, are estimated at $(1.4\text{--}1.7) \times 10^{12} \text{ t}$, and the initial extractable reserves, at $(420\text{--}510) \times 10^9 \text{ t}$. If to eliminate the "stored" (recovered) and "revealed" (explored, extractable) oil reserves ($100 \times 10^9 \text{ t}$ and $160 \times 10^9 \text{ t}$, respectively) from the rated value of oil resources, the nonexplored reserves can be defined at $(160\text{--}250) \times 10^9 \text{ t}$. Our rated "revealed" oil reserves ($160 \times 10^9 \text{ t}$) computed for the OGB sedimentary cover are comparable with the data of Ronov ($124 \times 10^9 \text{ t}$) related to Upper Jurassic–Neogene clays.

CONCLUSION

The estimation of prognostic oil resources on the genetic basis is of interest in prospecting for oil both in separate oil- and gas-bearing basins and in their local sectors. Numerous geochemical investigations carried out with the use of modern methods of analysis of dispersed OM in rocks with different degree of secondary transformations during lithogenesis provide a quantitative determination of the productivity of oil source units. Based on such computations and taking into consideration the structures revealed in oil- and gas-bearing

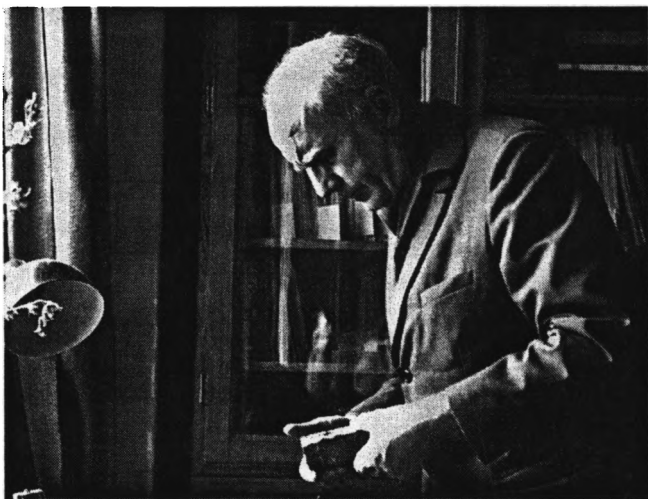
ing basins, it is possible to evaluate the potential of their local sectors. The computation executed on generation of HC in sedimentary rocks of such basins in the world, with regard only to clayey oil source rocks at the intermediate mesocatagenetic stage (MK₁–MK₃) and OM concentration of 0.5–3.0%, showed that nonexplored oil reserves can be appraised at $(160\text{--}250) \times 10^9$ t. This allows us to be optimistic with respect to prospecting for oil in the 21st century.

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CHRONICLE

In Memory of G.F. Krasheninnikov



November 18, 1999 would be the 90th birthday of Prof. Grigoriy Fedorovich Krasheninnikov, Honored Scientist of the Russian Federation, eminent lithologist, teacher, and active member of the Editorial Board of *Lithology and Mineral Resources*, where he happily and successfully worked until the end of his life (March 29, 1992).

Krasheninnikov's biography illustrates the life of a selfless intellectual and scientist who devoted his life to the vocation of science and retired his knowledge and wealth of experience to young geologists. He was the son of a biologist, who was himself a follower of academician K.A. Timiryazev. From 1927 to 1931, Krasheninnikov studied at the Moscow Geological Prospecting Institute. He started his work in the Transbaikalian region as a geologist. In 1931–1935, he headed a geological team of the East Siberian Geological Department and in 1935 joined the All-Russia Institute of Mineral Resources (VIMS) as a researcher and supervisor of "Lithology of Mesozoic Deposits in the Urals." Simultaneously he delivered lectures at Moscow State University (MGU) and left the institute in 1949 to accept a regular post at the university.

During World War II, Krasheninnikov took part in geological prospecting in the Chelyabinsk coal-bearing basin, which provided the defence industry with fuel. The work served as a basis for his PhD dissertation, which he defended in 1942. His formulated recommendations were widely used in prospecting and exploration work in coal-bearing basins of Siberia, the Urals, European Russia, Central Asia, and Kazakhstan. His DSc dissertation (1995) was devoted to "conditions

under which coal-bearing formations accumulated on the USSR territory."

Thus, Krasheninnikov became one of the founders of the theory of coal-bearing formations. Still, the field of his scientific interests was much more extensive. He developed a genetic approach to lithology and carried out paleogeographic studies on a wide range of old sedimentary deposits in platforms and geosynclines. He formulated his own scientific credo in the text-book *Theory of Facies* (1971), then later in *Theory of Facies with Fundamentals of Lithology* (1988), and in 170 papers and abstracts of papers.

Krasheninnikov was a contemporary and follower of Prof. M.S. Shvetsov and Academician N.M. Strakhov, founders of the science of sedimentary associations in the Soviet Union. His scientific and teaching activities left an appreciable trace in developing the school of lithologists at Moscow State University. Working as a professor of the Geological Faculty, he founded a laboratory at the Department of Historical and Regional Geology in 1956 and headed it until 1983, when a new Department of Lithology and Marine Geology was created. The department was headed initially by P.P. Timofeev, Corresponding Member of the Russian Academy of Sciences, and since 1990 by Prof. O.V. Yapaskurt, Member of the Russian Academy of Natural Sciences and disciple of Krasheninnikov. During the 25-year period, Krasheninnikov elaborated two fundamental courses ("Lithology" and "Theory of Facies") and delivered lectures to students of geology and geography, as well as supervised 32 PhD and four DSc dissertations related to geological and mineralogical sciences.

During this period, he conducted scientific research in the Donetsk basin, central Kazakhstan, and northern Yakutia. Krasheninnikov and his students realized a single methodological concept according to which the study of sedimentary rocks and their associations is independent of the nature of problems facing geologists. Whether the problems are theoretical or applied, the methodology follows three fundamental principles, namely, genetic, historical, and systematic approaches to cognition of natural objects.

Krasheninnikov's ideas and investigations earned him immense prestige among the Russian and international scientific community. His lectures and papers were noted for their scientific novelty, great erudition and wide range of perspective. Krasheninnikov represented Russian Science at international forums. He participated in sessions of the International Geological

Congress in Mexico (1956), India (1964), Canada (1972), and Australia (1976).

In 1979, he was awarded the title of an Honoured Scientist of the Russian Federation. The nomination was approved by scientific workers from many research institutes and universities.

Krasheninnikov contributed much to the Commission on Sedimentary Rocks of the Division of Earth Sciences, RAS. The Section of Sedimentary Rocks of the Moscow Society of Nature Explorers (MOIP), which he permanently headed, was his favorite creation.

Grigorii Fedorovich was fond of field work. Even in old age, he continued to explore distant and difficult to access localities, while giving students and young geologists lessons on caring about nature, as well as a strict and critical approach to the selection and interpretation of results from scientific observations.

The name Grigorii Fedorovich Krasheninnikov will forever remain in the scientific history of sedimentary rocks, in the history of our journal, and in the memory of his disciples and colleagues.

O.V. Yapaskurt

CHRONICLE

In Memory of A.K. Lisitsin



Anatolii Kuz'mich Lisitsin, DSc (Geol.–Miner.), main researcher of the Institute of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM) of the Russian Academy of Sciences, a notable hydrogeologist and geochemist, distinguished specialist in the field of rare metal–uranium deposits, tragically and unexpectedly passed away on March 8, 1999.

Lisitsin was born on November 23, 1928 in the Village of Beloz'er'e, Spas-Klepiki district, Ryazan oblast. In 1938, his family moved to the Biryulevo Settlement, Moscow oblast. He graduated from the Hydrogeological Faculty of the Moscow Geological Prospecting Institute in 1952. In the same year, he joined Expedition 1 of IGEM, Russian Academy of Sciences (then the USSR Academy of Sciences), an event that predetermined his later scientific activity.

His first steps in science were made under the supervision of reknowned hydrogeologist, Aleksei Ivanovich Germanov, with whom he studied exogenous–epigenetic uranium–rare metal deposits in Paleogene deposits of the Fergana valley. It might be well to point out

that in this work Lisitsin went further than his mentor. Already in his 50s, in parallel with hydrogeology and hydrogeochemistry, he tried to examine processes of ore formation as a result of interaction of water and host rocks. Additionally, he analyzed the composition of infiltrational ore-forming solutions with respect to the geochemistry and mineralogy of an ore-enclosing series. Such an approach, progressive for those times, predetermined the trend in the theory of epigenetic uranium–rare metal ore formation.

In 1957, Lisitsin defended his PhD dissertation entitled “Hydrogeochemical Conditions at Uranium Deposits in Paleogene Rocks of the Northern Fergana.” In 1973, he successfully maintained the DSc dissertation “Hydrogeochemistry of Ore Formation, based on Exogenous–Epigenetic Uranium Deposits.” A monograph with the same title was published by *Nedra* in 1975. Later, it was translated into Chinese. The monograph represented a new step in understanding the mechanism of hydrogenous rare metal–uranium ore formation. The problem of quantitative geochemical assessment of underground water (pH, Eh, concentration and forms of ore components) was elaborated in detail, the problem of phase composition of metal settlers was elucidated, and the role of microbiological processes in migration and concentration of uranium and trace-elements were shown.

In 1978, Lisitsin was elected to the post of Head of the Laboratory of Hypergenous Processes and Lithology in IGEM.

During the 1980s, in connection with the radical reconstruction of uranium geology, Lisitsin studied problems of radiogeocology, protective properties of the geological environment, and safety burial of radioactive wastes. He solved many of these problems by using the enterprise Mayak and other objects as an example. In 1997, Lisitsin was elected to the position of the main researcher in the Laboratory of Radiogeology and Radioecology, IGEM.

Lisitsin wrote more than 135 scientific works. He is the author and co-author of 8 monographs, about 70 papers in journals, 55 scientific reports, as well as the discovery of “The Phenomenon of Deep Penetration of Atmospheric Oxygen into the Hydrosphere.” Acquaintance with the scientific work of Lisitsin allows us to cast a picture in mind of a strict methodologist, a man boldly introducing “number and measure” into the theory and practice of geological investigations, and a con-

vinced proponent of the union of geochemistry and exact sciences.

Lisitsin was an active member of the Section of non-ferrous and rare metal ores of the Interdepartmental Lithological Committee, a member of the Scientific Council of Expedition 1 of IGEM and VIMS (All-Russian Institute of Mineral Resources). From 1969 to 1981, he was a member of the Editorial Board of *Lithology and Mineral Resources*.

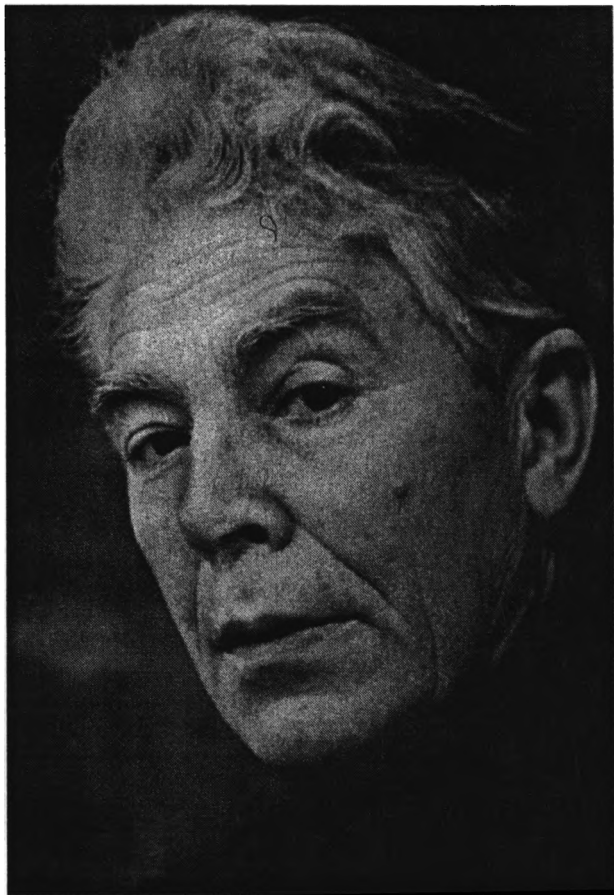
A fond memory about this outstanding scientist will forever remain in the hearts of his friends, comrades, and colleagues.

The staff of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences

Editorial Board of the Journal *Lithology and Mineral Resources*

CHRONICLE

In Memory of N.V. Logvinenko



Nikolai Vasil'evich Logvinenko, a prominent Russian lithologist, professor of St. Petersburg University, DSc (Geol.–Minerol.), and State Prize laureate, passed away on June 17, 1998.

His scientific activity began at Khar'kov University. After graduating from the Geological Faculty in 1937, Logvinenko studied coal-bearing deposits of the Donetsk basin. In 1941 he received a PhD (Geol.–Miner.), being among the first who defended a dissertation on lithology in the Ukraine.

During World War II, Logvinenko was engaged in the engineering-geological examination for constructing industrial enterprises in the Urals. After the war was over, he resumed his pedagogical and scientific work at Khar'kov University.

In 1947 Logvinenko defended his DSc dissertation devoted to the lithology and paleogeography of the productive Carboniferous sequence in the Donetsk basin. The dissertation represents an example of using the

composition of sedimentary rocks for the stratigraphy and facies–cycle analysis.

From 1947 to 1954, Logvinenko headed the Department of Geology at the Khar'kov Mining Institute. From 1954 to 1964, he headed the Department of Mineralogy and Petrography at Khar'kov University. During these years, he created the Khar'kov lithological school of young scientists, which became widely recognized.

The first monograph by Logvinenko, entitled *Lithology and Paleogeography of the Productive Carboniferous Sequence in the Donetsk Basin*, was published in 1953. The book immediately attracted interest of the geological community. The author established sedimentation cycles of different scale in Carboniferous deposits of the Donetsk basin. He also studied terrigenous and authigenous minerals and presented paleogeographical maps. The results obtained in the course of a Crimean expedition are the basis of the subsequent collective monograph *Lithology and Genesis of the Tavria Formation of the Crimea*.

The second stage of Logvinenko's scientific work is closely related to Leningrad (St. Petersburg) University where he founded and headed the Department of Lithology and Marine Geology for more than 20 years. During this period, Logvinenko prepared and published the text-book *Petrography of Sedimentary Rocks*, which was edited in 1967, 1974, 1984. This work was awarded the State Prize of the USSR and became a handbook for many lithologists and geologists.

Having taken part in the Pacific expeditions with R/V *Vityaz* and *Dmitrii Mendeleev*, Logvinenko then wrote the text-book *Marine Geology* which was published in 1980.

For many years Logvinenko elaborated upon the problem of secondary alteration of sedimentary rocks in continents and oceans. He identified parageneses of authigenous minerals for the catagenesis and metagenesis stages. He also described the platform and geosynclinal mineral facies and rock alteration zones, which are important for elucidating the geological evolution of regions. As a result of generalization of the work, the monograph *Formation and Alteration of Sedimentary Rocks in Continents and Oceans* was published in collaboration with L.V. Orlova in 1987.

The monograph, which was prepared together with I.S. Gramberg, Academician of the Russian Academy of Sciences, and entitled *Introduction to Geochemistry of Exogenous Processes* (1997) appeared to be his last prominent scientific work. The work reveals that pro-

cesses of exogenesis are biogeochemical. It also discusses the role of microorganisms in geochemical reactions in soils, weathering crusts, bottom sediments of lakes, seas, and oceans, as well as the effect of the exhalative, hydrothermal flow of a substance on the geochemistry of sediments and, in particular, the role of thermophile and barophile sulfate-reducing bacteria in the hydrothermal process. The book also emphasizes the role of the hydrothermal processes in formation of the salt composition in ocean waters.

Logvinenko was the editor and co-author of the "Lithology" section in the *Geological Dictionary* (1973, 1983), the editor and co-author of *Handbook of Lithology* (1983). He was the author of more than 250 papers, published in Russia and abroad, and about 20 monographs and text-books.

During his pedagogical work at Khar'kov University and St. Petersburg University, he supervised degree-level works of hundreds of geologists (litholo-

gists, marine geologists), as well as more than 10 DSc dissertations and 35 PhD dissertations.

Later in life, Logvinenko took up popular-scientific literature; he wrote the books: *The Joy of Learning* (1997), *University, My Love* and *I Love You, Crimea* (1998). Unfortunately, he did not see the last two books published. The works are permeated with a sense of love for life, knowledge, our planet, and university. Logvinenko possessed a great capacity for work, vital energy, curiosity, optimism, a sense of humour, as well as goodwill toward all people.

Nikolai Vasil'evich will forever remain in the hearts of his colleagues, students, and all who knew him, as a classic figure in Russian lithology, an eminent scientist and teacher.

N. S. Oknova, L. V. Orlova, and N. N. Verzilin

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